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PRINCIPAL METHODS AND APPARATUS FOR INVESTIGATING OXIDATION  
PROCESSES IN METAL AND ALLOYS

By D. V. Ignatov

- USSR -



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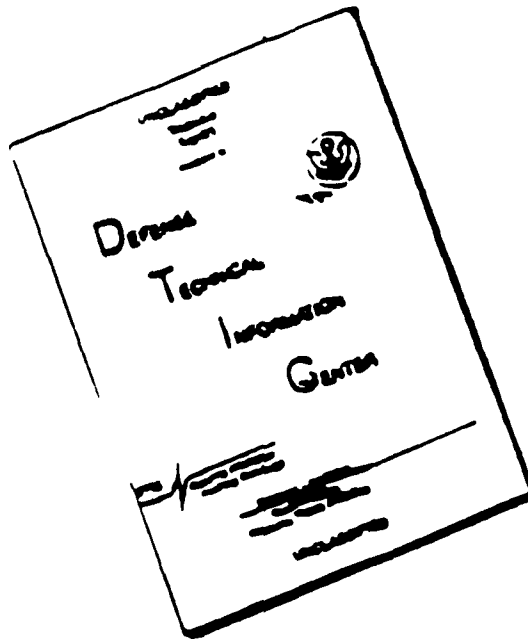
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PRINCIPAL METHODS AND APPARATUS FOR INVESTIGATING OXIDATION  
PROCESSES IN METAL AND ALLOYS

-USSR-

[Following is a translation of the article "Osnovnyye metody i apparatura dlya issledovaniya protsessov okisleniya metallov i splavov" (English version above) by D. V. Ignatov in Doklady Instituta Metallurgii imeni A. A. Baykov (Works of the Institute of Metallurgy imeni A. A. Baykov), No 5, Production Metallurgy, Physical Metallurgy and Physicochemical Methods of Research, Moscow, 1960, pages 202-237.]

As is known, the oxidation of metals and alloys is a complex crystallochemical and kinetic process embodying a number of other elementary processes. Its first stage is characterized by direct interaction of the metal with the oxidizing reagent and actually represents chemical adsorption (or, more exactly, physical adsorption, changing rapidly to chemical adsorption). For almost all metals and alloys this stage proceeds very rapidly even at room temperature and is completed in a few minutes. Depending on the nature of the metal, oxide films of a thickness equal to the size of one or two elementary cells of the lattice of the oxide corresponding to the given metal are formed on the surface (1). Since the metal-oxygen system is thermodynamically unstable (with the exception of gold) in a rather wide range of temperatures, including room temperature, the energy of activation of the oxidation process in this stage has little significance (by comparison with the heat of formation of the oxide). An indirect confirmation of this contention is the well known fact of the spontaneous combustion, upon rapid contact with oxygen, of the thin films of many metals obtained by the method of evaporation and condensation in a vacuum on non-heat-conducting supports. This phenomenon is also characteristic of freshly reduced powders. According to the available data, an activation energy of 9 kcal/mol is required to oxidize beryllium at room temperature (2), and 8.7 kcal/mol for molybdenum (3).

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Depending on the time, this stage is expressed quantitatively by the exponential law of oxidation (with exception of such metals as sodium and calcium, for which the linear law is observed already at room temperature). With the formation on the surface of the metal of an oxide film 10-15 Å thick, the oxidation process proceeds very slowly and practically stops. For example, in aluminum the oxide film of this thickness is formed after a few minutes at room temperature, whereas its further growth to a thickness of 40-45 Å takes 40-90 days (1). The sharp diminution of the rate of the oxidation process in this stage is to be explained by the fact that the oxygen does not interact with the metal directly, since the reacting elements -- metal and oxygen -- are separated by the oxide film. The metal and oxygen atoms (or ions) have to pass through the oxide film to get into contact and react with one another. For this, they have to possess such a supply of kinetic energy as will permit them to overcome the binding forces between the metal and oxygen ions of the lattice of the oxide formed by the conversion of the free energy of the metal-oxygen system in the first stage. This energy supply at room temperature is possessed by only a very small part of the atoms of the system, in accordance with Boltzmann's well-known law of distribution. Hence, the oxidation process in this stage, called the secondary, proceeds very slowly and practically ceases upon formation of an oxide film of a certain maximum thickness on the surface of the metal. For most metals, such films have a thickness of  $\sim 50$  Å for room temperature and are a protection against oxidation up to 200-400°. Thus, the oxidation process in the secondary stage does not occur without additional energy (activation energy).

The oxidation process is activated with comparative ease by heating the whole system or by activating its gaseous component, for example oxygen. In the first case, principally the metal and the oxide phase are activated, since the binding forces between the atoms or ions in the lattices of the solid phases weaken with the growth of temperature and the coefficients of diffusion of oxygen as well as through the oxide film increase. In the second case, principally the gaseous component is activated by an electric discharge or the irradiation of the gas by a stream of electrons, protons, etc. This action produces active particles of oxygen: ions  $O^-$ ,  $O_2^-$ ,  $O_2^+$ ,  $O^+$ ; atoms; and excited molecules. In the activated oxygen, with the aid of a glow discharge (4-9) some metals (especially the precious ones) oxidize very intensively at 40-100° on the anode of the discharge tube: in 30-40 minutes. With a current density of 1-2 ma/sq cm aluminum films 300-400 Å thick oxidize completely, and silver films of the same thickness oxidize completely in a few seconds.

The rate of oxidation of a metal upon heating is determined by the following basic factors:

- 1) The crystallochemical correspondence between the lattices

of the metal and the oxide;

2) The parameters of diffusion of the ions of the metal or oxygen through the oxide film (depending on the type of semi-conductor to which the oxide of the given metal belongs);

3) The phase and chemical conversion in the skin (especially in the case of many-layered oxide films); and

4) The phase and other conversions in the metal itself.

The rate of oxidation is also affected by such factors as tensions arising in the dross owing to the different volumes of the metal and the corresponding oxide; the recrystallization processes in the dross; the rise of textures; the physicochemical properties of the oxides (stability, volatility, melting point, expansion coefficients); porosity, plasticity and cohesion of the dross with the metal.

In the case of alloys (especially those with many components) the following are to be added to these oxidation factors: the thermal activity of the alloy components, which determines the ion concentration in the several alloy components at the alloy-dross boundary; the diffusion parameters of these components through the dross; the secondary oxidation and reduction reactions in the dross at the alloy-dross boundary; the reactions between the oxides of the several components of the dross type --  $\text{NiO} + \text{TiO}_2 = \text{NiTiO}_3$ ,  $\text{NiO}_2 + \text{Al}_2\text{O}_3 = \text{NiAl}_2\text{O}_4$ ; the decomposition of oxide compounds at high temperatures and the evaporability of some of them.

As may be seen, the oxidation process is governed by many factors even in those cases where the metal is not under conditions of simple [single?] or cyclic stress and is likewise not subjected to the action of heating with different frequencies of heat exchange and in various corrosive gaseous media. Hence, in order to examine the oxidation process more broadly and deeply, and in general to study the mechanism of the interaction of metals with gases, it is necessary to employ a number of methods of physicochemical analysis.

The oxidation process of metals at the temperature interval from  $20^\circ$  to the temperature close to the melting point proceeds according to the following time laws (of the dependence of the growth in weight  $\Delta p$  upon the time  $t$ ):

1) The exponential or logarithmic law:  $\Delta p = K \ln (\text{at } +1)$ , at temperatures from  $20$  to  $200-400^\circ$ ;

2) The cubic law:  $(\Delta p)^3 = Kt + c$ , at  $400-500^\circ$ ;

3) The parabolic law:  $(\Delta p)^2 = Kt + c$ , for temperatures above  $500^\circ$ ; and

4) The linear law  $\Delta p = Kt + c$ , at high temperatures. These intervals of temperature are conditional, since they are different for each metal.

The constant  $c$  in the last three equations determines only

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the presence of an oxide film on the surface of the metal for the moment of time  $t = 0$  -- for example, its formation in mechanical (grinding) or chemical (electric polishing) working of the surface of the sample. The thickness of this original oxide film is small (up to  $100 \text{ \AA}$ ), hence it can be disregarded in determining the rate of high-temperature oxidation. The constant  $K$  in these equations characterizes the rate of the oxidation process and is its basic parameter.

In most cases the rate constant  $K$ , depending upon the oxidation temperature, is expressed in the form of Arrhenius's equation:

$$K = A \cdot e^{-\frac{Q}{RT}},$$

where  $A$  is a constant whose dimension is determined by that of  $K$ ;  $Q$  is the energy of activation of the oxidation reaction.

It follows from this equation that  $\ln K$ , depending on  $\frac{1}{T}$  is a linear function. Hence, having constructed a graphic with the coordinates  $\ln K - \frac{1}{T}$  from the experimental values of  $K$ , it is possible to determine the activation energy of the oxidation process  $Q$  from the tangent of the angle of inclination of the straight line.

The activation energy is the basic energy parameter characterizing the oxidation reaction from the quantitative aspect (determine the strength of the binding forces in the lattices of the oxide and metal).

By comparing the values of the rate constants and energy of activation for the various metals in the comparable interval of temperature, it is possible to give an evaluation of their heat resistance at this or that temperature and of their suitability for practical use.

In cases where the experimental data deviate substantially from this or that law (mostly the parabolic law for high temperatures) of oxidation, the intensity of the oxidation process is characterized by the weight method by determining its mean rate during a definite interval of time for a given temperature. This is what is usually done when tests are made of the heat resistance of alloys in lengthy rustings and in determining durations of serviceability.

Data on the rate constants and the activation energy of the oxidation reaction of metals can also be obtained by the manometric method from the change in the pressure of oxygen in the reaction vessel owing to the absorption of oxygen by the oxidizing metal.

A substantial defect of both these methods is that in using them to determine the oxidation rate it is necessary to know the true surface area of the sample, which changes during the oxidation process. Hence, in practice, the growths in weight are related to the area of the visible surface and corrections are sometimes introduced by multiplying the geometric area by the coefficient of roughness, which is

numerically equal to the ratio of the true surface to the geometric surface area of the sample.

The true surface area is determined from special experiments with the adsorption of argon (or other inert gas) at the temperature of liquid nitrogen (10). For a polished surface, this coefficient is 2, but for thin films of metals obtained by the method of evaporation and condensation in a vacuum, it may vary from 2-20 or more, depending on the melting point of the metal and the rate of evaporation. According to electronic microscopy and electronography data, the dimensions of the crystallites in the thin films of such easily fusible metals as magnesium and aluminum are 200-300 Å, and for such metals as titanium and chromium, 20-30 Å, i.e., 10-15 times smaller. Of probably the same order will be the relationship between roughness of the films of metals condensed on a cold underlay (podkladka), depending on their melting point. The roughness coefficients of the surface of etched samples or of their surfaces obtained by reducing oxides with hydrogen have values from 20-1000, depending on the methods of etching and reduction (11).

However, in high-temperature oxidation the original roughness of the surface disappears during the first few hours of oxidation, depending on the heating temperature. Thus for example, in our experiments the roughness of the surface of the samples of nikhrom [a nickel-chromium-iron] alloy, resulting from polishing on 4/0 emery paper, disappeared after 5 hours of heating at 600° and 2-3 hours at 800-900°. Hence, the effect of the original roughness on the oxidation rate may be disregarded in protracted oxidation, for example, 25-50 hours. The change in the degree of roughness in the oxidation process is one of the causes of the diminution, observed in our experiments, of the values of the rate constant of this process depending on the time at a constant temperature.

In some cases practical workers use a number of other methods, by which they judge the oxidation rate from the thickness of the oxide (and other) films forming on the surface of metal samples, depending on the temperature and time of heating. To these methods belong:

- 1) Optical -- from the change in coloring (interference), from the change in the coefficient of ellipticity from thickness (polarization), and from the change in the original intensity of light from thickness owing to adsorption;
- 2) Electric -- from the change in electro-conductivity; and
- 3) Electrochemical -- from determination of the amount of electricity needed to reduce the oxides.

All these methods, described in sufficient detail in (12, 13, and 14), are also applicable to comparatively thin films of oxides in cases where the optical or electric constants of the forming oxides are known.

Thus, with the aid of kinetic methods it is possible to deter-

mine the two basic parameters of the oxidation process: the rate constant, or average oxidation rate, and the activation energy of this process. However, on the basis of data on these parameters alone, it is not possible to explain the mechanism of the oxidation of metals and alloys and to solve the questions concerning their protection from gas corrosion. Hence, alongside of kinetic methods, it is necessary also to apply analytic methods:

- 1) Chemical analysis;
- 2) Structural analysis (radiographic, electrographic, neutronographic, metallographic, and electron-microscopic; and
- 3) Isotopic methods (methods involving radioactive and stable isotopes).

Supplementary methods permitting one to determine the physico-chemical properties of metal and oxide systems and first and foremost the bond energy in their lattices are the thermographic and colorimetric methods of determining the energies of sublimations and activities, as well as of the character of conductivity (determination of the Hall coefficient) and the coefficient of thermal expansion.

Below is given a description of the weight, structural (except radiographic and neutronographic) and isotopic methods of investigating the process of oxidation of metals and alloys.

#### WEIGHT METHODS

By means of weight methods the oxidation rate at a given temperature is determined either by the growth in weight or by the loss of weight of the sample (in the case of volatile oxides or under operating condition) per unit of time and per unit of its geometric surface. The weight increase of samples in the oxidation process is determined by continuous or discontinuous weighing.

The method of determining the oxidation rates by loss of weight, as well as the results of investigation as to gas corrosion in various gaseous media and under various conditions of cyclic loading of the sample, are described in (15 and 16). The weight increase of samples due to oxidation, when weighed either continuously or discontinuously, is determined on an ordinary microanalytic balance with a sensitivity of  $2 \cdot 10^{-5}$  g per graduation of the optical scale of the reading microscope.

As a rule, the sample during the whole experiment should be in one and the same crucible, tempered to a constant weight at a temperature 200-250° higher than the maximum temperature of investigation. It is best to use thin-walled corundum crucibles, which have a small weight and acquire a constant weight when tempered for 4-50 hours at 1350°. Only in cases where it is known that the oxide films do not peel off of the samples and do not crumble is it possible not to use crucibles in heating samples.



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Each of the methods of continuous or discontinuous weighing has its positive and its negative sides. In discontinuous weighing it is possible to charge the furnace simultaneously with several samples (20-25), which is very important both for obtaining the mean values of the weight increase and for the integrated investigation of the oxidation mechanism as a whole. This method can be used to determine more accurately the surface temperature and weight increase of the samples than in the case of continuous weighing. But its essential defect is that in cyclic heating and cooling, the dross in some cases peels off of the sample partially or entirely as a result of mechanical shearing tensions. The latter are set up in it by the different coefficients of thermal expansion, as well as by the different volumes of the metal and the corresponding volume of the oxide. After each heating and before weighing, the samples in the crucibles should be cooled and kept in a drier with calcium chloride or some other absorber of water vapor. All the weighing operations are especially complicated if the experiments relating to oxidation are made in pure oxygen.

In continuous weighing, the sample during the whole experiment is not taken out of the reaction tube or electric oven when oxidized in air. The change in weight is read periodically at specific intervals from the scale of the measuring microscope or is recorded by a photoelectric recorder and an electronic potentiometer (one of the successful systems of recording weight change is described in [17]). The main difficulty in weighing in this case is that of eliminating vertical and horizontal oscillations due to displacement of air (or oxygen), and also to vibrations caused by compressors and pumps. By eliminating vibrations and oscillations in the weighing installation when using the self-recording system of weight change in samples it is possible to obtain the kinetic curves of oxidation of metals considerably more rapidly than by discontinuous weighing. It is more advisable to make the continuous-weighing installation hermetic, which will permit experiments relating to oxidation in pure oxygen or in some other gaseous oxidizing medium of prescribed composition.

In continuous weighing, the oxidation rate of the sample is not affected by the factor of alternate heating and cooling, which results in cracking and peeling of the dross. However, under real conditions, articles of metals or alloys are used under cyclic temperature regimes. Hence, in evaluating the corrosion resistance of this or that material, one cannot base one's conclusions solely on the data on their oxidation rates obtained by the continuous weighing method. Moreover, in ascertaining the oxidation mechanism, such factors affecting the rate of reaction as the peeling of the oxide film during alternate heating and cooling must be eliminated. It is evident that only by applying both these methods to one and the

same objects can one obtain fuller and more reliable data both on the rate constants of the oxidation process and on the heat resistance of the materials investigated.

In view of the fact that the discontinuous weighing method permits simultaneous experiments in the oxidation of metals with many objects, one can choose such a quantity of samples as to combine the processes of continuous and discontinuous oxidation.

For this purpose, and to investigate the determination of the structure and composition of the dross, it is necessary to prepare 22 samples entirely alike in composition and degree of surface roughness. Then, proceeding from the calculation that in an experiment lasting 25-50 hours it is necessary to obtain 8 points to construct the kinetic oxidation curve on weight-growth and time coordinates, one can take out and weigh five samples after definite intervals of time. Thus, for each point of the kinetic curve, five weight-growth values will be obtained, three of which are for samples of discontinuous oxidation and two for samples of continuous oxidation. The last two samples are then used for the electronographic and metallographic investigation of the microstructure of that point. Furthermore, the dross of these samples can also be used for its chemical analysis. Three of the 22 samples will oxidize continuously for 25 or 50 hours. To construct the graph and determine the value of the activation energy it is necessary to determine the value of the rate constant for various temperatures. Consequently, 88 samples are required for a full kinetic and structural investigation at four heating temperatures.

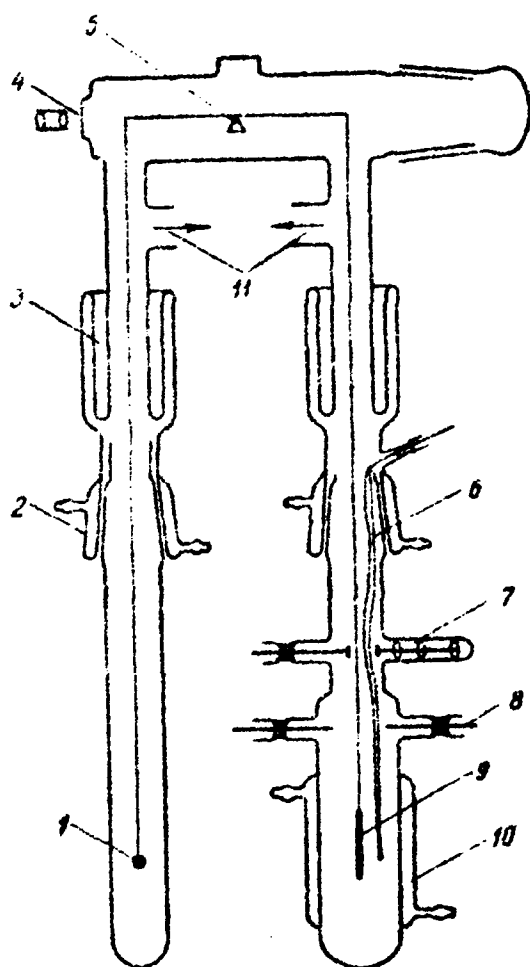
A peculiarity of this method is that it makes it possible to obtain for the points of the experimental kinetic oxidation curve data on the mean oxidation rate, the phase and chemical composition of the dross, and also on its microstructure. Ordinary muffle furnaces may be used to heat the samples in air. In heating in gaseous media of the prescribed composition, it is more advisable to employ cylindrical horizontal furnaces, in which it is convenient to heat the reaction tube (up to 80 mm in diameter and one meter long). The latter is usually made of quartz or synthetic mullite and zirconium. Slides or couplings of "pyrex" glass are used to connect with pumps and other devices of molybdenum glass. The furnace should be sufficiently long in extent and have a constant temperature. It is best to place the crucibles in a plate (or quartz or the oxides  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$ ) with apertures for them. Here it is necessary to see to it that no particles of extraneous matter adhere to the crucibles and that the weight has not been increased through interaction between the crucibles and the material of the underlay. The best material for underlays (or bushing in the form of rings) for the crucibles in this case is platinum. The sample should touch the walls of the crucible only at a few points. This condition is easy to fulfill if it is inclined to

the vertical axis of the crucible. Samples can be shifted from the cold zone to the hot zone of the tube by means of an electromagnet.

#### METHOD OF CONTINUOUS WEIGHING ON A TORSION BALANCE

It is especially advisable to employ the continuous weighing method in cases where the kinetics of the interaction of metals with pure oxygen (or other gas) is being investigated, beginning with the primary stage of adsorption and ending with the formation of the chemical compounds. In this case, a torsion balance with a sensitivity of  $10^{-7}$  to  $10^{-9}$  g is commonly used (Fig. 1).

(Note: Yu. N. Lebedev took part in mastering the use of this balance.)



#### Legend:

- 1) Counterweight; 2) water-cooled slide; 3) trap to be filled with liquid nitrogen; 4) window with plane-parallel walls for reading deflections of beam; 5) beam support;
- 6) thermocouple; 7) movable electric contact; 8) electric current leads;
- 9) sample; and 10) refrigerator.

Figure 1. Scheme of Vacuum Torsion Balance

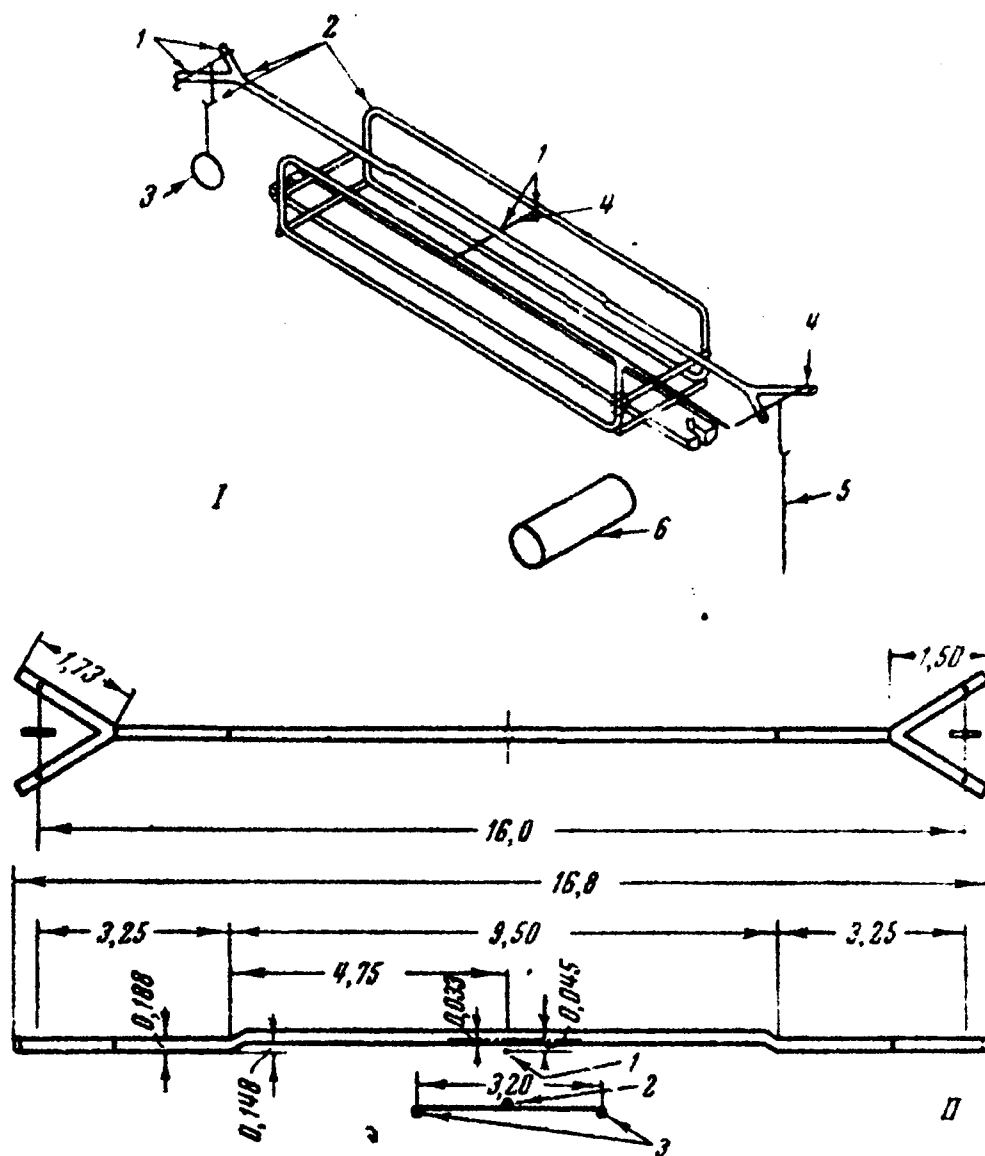


Figure 2

Legend: I (top) -- Supporting Frame: 1) Solder of AgCl; 2) fused quartz; 3) counterweight; 4, 5) tungsten wires 25 and 50  $\mu$ k in diameter; and 6) reading microscope.

II (bottom) -- Beam: 1) Center of gravity of beam; 2) beam; and 3) supporting frame.

It consists of two identical vertical glass tubes welded together by a third horizontal one in the form of the Cyrillic letter **П**. In the horizontal tube is placed the frame with the twisting tungsten filament welded to it, and with the beam welded to the middle of this filament. The frame and beam are made of quartz, and the welding is done everywhere with silver chloride. The beam is usually made of bars of fused quartz of a constant diameter throughout their length.

The beam, 150 mm long and 2 mm in diameter, is welded so that its center of gravity is 0.20-0.30 mm lower than the point of support. This is accomplished by bending the quartz bar at two points symmetrically distant from its geometric center; the point of support of the beam and the points of suspension of the filaments bearing the sample to be weighed and the counterpoint should lie in the same plane (Fig. 2). Horns are welded to the ends of the beam and a tungsten filament is soldered to them. Hooks for suspending the sample and counterweight are fastened to the middle of this filament by means of silver chloride. The hooks and filaments for the suspension are made of quartz. The horizontal tube and one-third of the length of the vertical tubes can be made of molybdenum glass; the remainder of the tubes are made of quartz or fused aluminum oxide. The coupling between the quartz part of the tube and the molybdenum tube is made either with a special glass composition having a thermal-expansion coefficient intermediate between quartz and molybdenum glass, in the case of whole tubes, or these parts of the tubes are united by means of slides. The lubricant vapor of the slides is frozen out by liquid air poured into a special trap over the slide (see Fig. 1).

In the vertical tubes are placed metal diaphragms which, having small apertures through which to pass the suspension filaments for the sample and counterweight, reduce the intensity of the convection currents during the experiments at high temperatures. They furthermore promote the cooling of the hot masses of air, since there are traps with liquid air and running water circulating around them at the places where these diaphragms are located.

The whole glass part of the weighing assembly, with a high-vacuum oil diffusion pump, measuring lamps and a flask for oxygen, is mounted on a massive steel frame soldered to a steel plate 3 cm thick and 70 X 80 cm square. To protect the balance from vibration, tennis balls (about 100) are used, on which the plate of the weighing assembly is set. A microporous rubber mat is placed under the pre-vacuum (forvakuunnyy) pump, and a rubber coil uniting the pump with the balance is firmly fastened to the wall. However, it is difficult to eliminate vibration entirely, especially in weighing in a high vacuum ( $\sim 10^{-6}$  mm of mercury). In this case, the pre-vacuum pump is turned off during the experiment, and the high-vacuum diffu-

sion pump exhausts into a previously evacuated spare flask (up to  $10^{-3}$  of mercury). The high vacuum can be maintained in the system by turning off both pumps with the aid of traps filled with activated carbon and cooled with liquid nitrogen. Titanium or zirconium in the form of a wire or foil can be used for this purpose. Both these metals absorb large quantities of nitrogen and oxygen when heated to  $700-800^{\circ}\text{C}$ . In reaching a high vacuum ( $10^{-6}\text{ mm}$ ), the unit should be flushed several times with an inert gas (argon of spectral purity). In this case the gases and the water and lubricant vapors given off from the several parts of the unit, especially from the tolerances, are removed more quickly. Furthermore, the residual gas in the apparatus at a pressure of  $10^{-6}\text{ mm}$  will be an inert gas. Such precautionary measures have to be taken in obtaining fine layers of metal in a vacuum and using them subsequently as objects for examining the adsorption or oxidation processes, as well as in cases where the rate of evaporation of the metals is being determined.

The basic parameters of the torsion balance are sensitivity, vibration period, and limit weight of charge, which can be determined on the balance with controlled precision. These basic parameters are closely related to one another, so that a change in one of them causes a change in another. Hence, in choosing this or that balance design, one is governed chiefly by what problems it is intended to solve. If, for example, the problem is posed of investigating the oxidation mechanism of any metal, beginning with the adsorption stage, then the weight of a one-molecule layer of oxygen equivalent to  $3.51 \cdot 10^{-6}\text{ g}$  for an area of  $1\text{ sq cm}$  must be determined on the balance.

The basic parameter of the equal-armed beam balance -- the sensitivity -- is determined by the ratio of the angle of deflection of the beam to the overload  $\Delta p$ , which produced this deflection, i.e.,

$$\alpha = \frac{\Delta \varphi}{\Delta p} \text{ radian/g.}$$

In this expression, the ratio of the displacement of the beam, determined from the scale of the measuring microscope, to the length of the arm  $l$  of the beam, may be substituted for the angle (because of its small size):

$$\alpha = \frac{h}{l \Delta p},$$

where  $h$  is the displacement of the beam.

Hence, in practice the sensitivity of a given balance (with proscribed  $l$ ) is determined by the size of the displacement of the beam relative to the size of the overweight causing this displacement. In most cases the sensitivity of the balance is expressed in grams per graduation of the microscale of the measuring microscope, which in ordinary microscopes with a micro-ocular attachment, corresponds

to 10 mk.

Instead of this microscope, an OMG-6 microscope with a 1 mk. graduation value can be used. Such sensitivity is determined experimentally from the straight line of graduation. For this purpose, batches of 0.1, 0.2, 0.3 mg, etc., weighed with precision on the microanalytic balance, are taken and suspended from one of the ends of the beam, and the size of the displacement of the other end is found with the aid of the microscope. The value of  $\Delta p$  is determined from the straight line of graduation by dividing the weight of the charge by the number of scale units of the displacement of the beam on the microscope scale. To make a balance with a sensitivity of  $2 \cdot 10^{-7}$  g, with an oscillation period of 3 seconds for a sample weighing 0.5-0.8 g, it is necessary to make a beam 15-16 cm long of fused quartz in the form of a bar 1.3-2 mm in diameter. A tungsten wire 25 mk in diameter and 25-30 mm long should be used as supporting filaments. The distance from the point of support to the center of gravity should be 0.3-0.4 mm. The threshold of sensitivity may be lowered to  $10^{-9}$  g by diminishing the weight of the sample to some tenths of a milligram, making the diameter of the support filaments 5-10 mk and bringing the distance from the center of gravity to the point of support down to 0.10-0.15 mm.

Quartz filaments, which are more stable with respect to temperature changes, are often used instead of tungsten filaments. However, it is hard to prepare them and still more difficult to assemble them.

While it is comparatively easy to achieve great sensitivity in the balance, it is considerably harder to attain great precision in weighing, inasmuch as the precision of the determination of change in the weight of the sample in its oxidation process for any ideally designed balance is affected by three basic factors: vibration, change of temperature, and pressure in the balance space and the suspended charges.

The effect of vibration can be completely eliminated in only two ways. One of them is to keep the balance beam with the support frame and suspended loads in the weighed state, for example, by a field (as in the case of melting metals without a crucible) within the casing or reaction tubes of the balance. Another method consists, on the other hand, of creating a firm mechanical connection of the whole structure of the balance with the mass of the ground. For this purpose, the massive pedestal or substructure of the balance must be let into the ground to a depth considerably greater than the foundation of the building itself and the substructure of the compressor and pumping installations. Our experiment in using tennis balls and massive support plates to absorb vibration, as well as in replacing pumps for maintenance of a permanent vacuum in the weighing installation by gas-absorbing materials, has yielded positive results.

As a very simple means of protecting the balance from oscillations of great amplitude, which may result from resonance or the accidental rapid admission of gas into the balance space, it is useful to restrict the movement of the beam by two slightly taut wires of tungsten 25-30 mk in diameter welded to the two sides of the beam at a distance somewhat greater than the deflection of the beam that is the maximum admitted by the scale of the reading microscope.

The effect of the temperature factor is determined by calibrating the balance for each working temperature. The correction coefficient determined from these calibration lines with a balance sensitivity of  $3 \cdot 10^{-7}$  g should be  $6 \cdot 10^{-7}$  g/°C. To reduce the effect of the temperature factor the part of the balance in which the beam with the supporting frame is located is put into an air thermostat, in which the temperature is kept somewhat above room temperature.

The pressure factor affects the change of weight in the sample and counterweight due to buoyancy. To eliminate it, the sample and counterweight should be made of one and the same material, and the counterweight should differ from the weight of the sample by 0.2%. With identical values of weight and volume, the sample and the counterweight must have entirely different surface sizes. Hence, the counterweight must be made in the form of a ball with an ideally polished surface, and the sample in the form of a sheet-iron or foil plate with a surface of 10 or 100 times larger than the surface of the counterweight. In determining the quantities of gases absorbed by the sample, a correction must be made for the absorption of the gas by the counterweight.

The conditions of operating the balance are considerably complicated in investigating the kinetics of the oxidation of metals at raised and high temperatures. On the one hand, it is necessary to place both ends of the beam and the sample with the counterweight under identical temperature conditions in order to reduce the effect of the temperature factor and convection. On the other hand, the samples with their counterweights must be of one and the same material in order to eliminate the effect of buoyancy. In this case, one endeavors to select a counterweight of oxides of the same density (as, for example, quartz in the oxidation of aluminum) or a counterweight of the same material is welded into a thin-walled quartz tube. Or, finally, the upper part of the balance, in which the supporting frame with the beam and counterweight is located, is placed in a thermostat and the balance is graduated for each working temperature. Allowing for these corrections, a change of  $10^{-7}$  g  $\pm$  20% and  $10^{-6}$  g  $\pm$  10% in the weight is observed when the zero position is stable.

To remove charges from the walls of the horizontal and vertical tubes (especially when the suspension filaments, the support filaments, and the tubes themselves are made of quartz), their inner surface is covered with a thin platinum film, which is grounded.



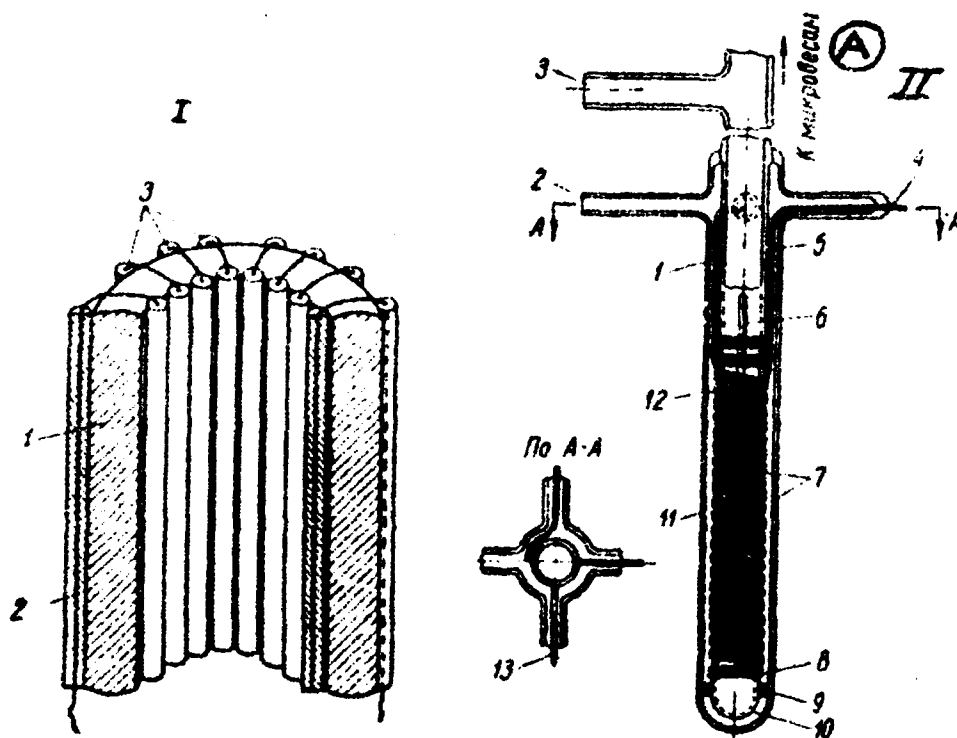


Figure 3

Legend: I (left) -- Type of Winding in Which No Magnetic Field is Produced: 1) Porcelain cylinder; 2) wire 1.2 mm in diameter of Karmilov alloy; 3) thin porcelain tubes.

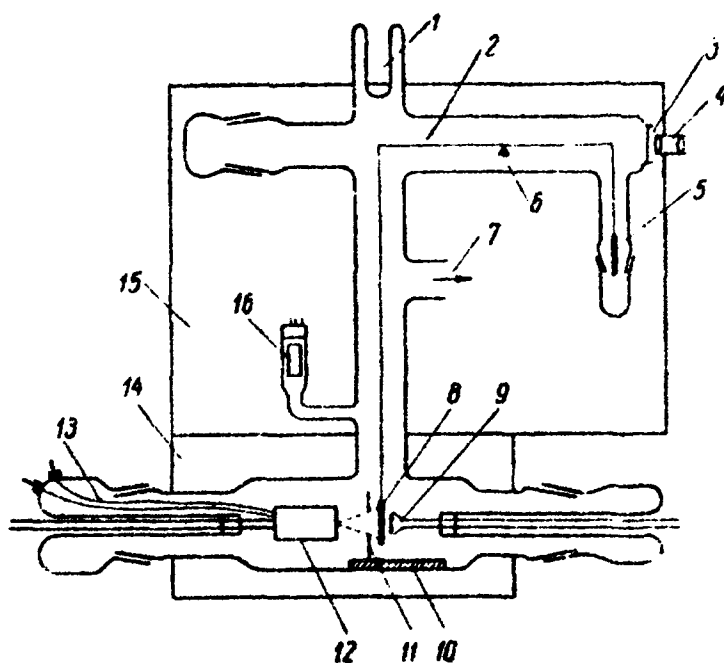
II (right) -- Vacuum Heating Furnace of Molybdenum Tape: 1) Weld of "pyrex" glass with porcelain; 2) exhaust for evacuating the outer jacket; 3) exhaust for evacuating the inner tube; 4) lead-in of tungsten wire; 5) multi-strand lead-in wire of nickel; 6) platinum-platinorhodium thermocouple (10% rhodium); 7) MacDaniel porcelain (synthetic mullite); 8) molybdenum tape; 9) distance ring of alundum; 10) inner tube; 11) outer tube; 12) heater with bifilar winding of molybdenum tape; and 13) platinum-platinorhodium thermocouple.

(A) =  $\pm$  to the microweight

Cylindrical furnaces with bifilar winding or with the winding shown in Fig. 3, I. are used as heating elements.

The temperature of the sample is measured with a thermocouple, the ball of which is in contact with the other sample exactly like the one being weighed, and is located as near as possible to the latter.

The reaction tube is most simply manufactured from quartz. But quartz, beginning at  $800^{\circ}$ , conducts oxygen; hence, for experiments in the temperature interval  $800-1000^{\circ}$ , it is necessary to use a tube with double walls, and the air must be pumped out of the space between them. A model of such a tube with a heater of molybdenum tape installed between its walls is shown in Fig. 3, II (19). At temperatures of  $1000-1400^{\circ}$  the best material is aluminum oxide ( $\alpha - \text{Al}_2\text{O}_3$ ) and also  $\text{BeO}$ . These oxides undergo no phase conversions and do not possess any noticeable evaporability in this area of temperatures. The oxide compounds of the  $\text{NiAl}_2\text{O}_4$ ,  $\text{ZrSiO}_4$ ,  $n\text{SiO}_2$ ,  $m\text{Al}_2\text{O}_3$  type decompose in a vacuum at temperatures above  $1300^{\circ}$ .



Legend: 1) Trap for liquid nitrogen; 2) quartz beam; 3) plane-parallel glass; 4) reading microscope; 5) counterweight; 6) support (place where beam is soldered with tungsten filament); 7) evacuation tap; 8) target; 9) outlet for heating target in degasification; 10) massive copper plate for cooling collimator; 11) collimator; 12) evaporator; 13) thermocouple; 14) water cooling; 15) air thermostat; and 16) ionization lamp for measuring vacuum.

Figure 4. Scheme of Vacuum Microbalance for Determining Heat of Sublimation and Activity of Components of an Alloy

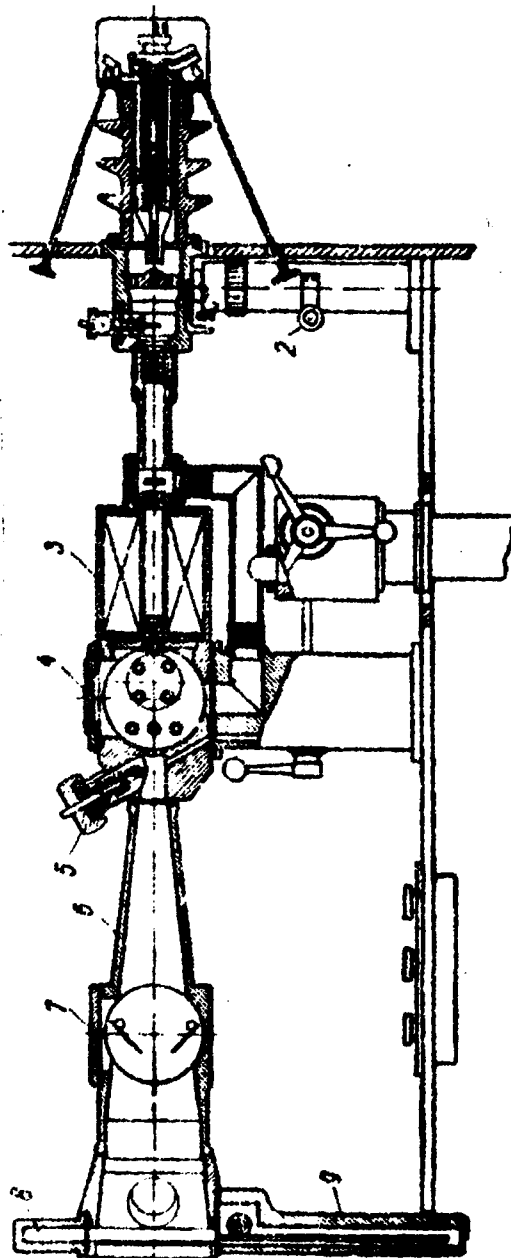


Figure 5. Design and Arrangement of the Main Nodes  
of the EG Electronograph

Legend: 1) electron gun, fastened to stand 2; 3) electromagnetic lens;  
4) camera and sample holder; 5) intermediate valve, separating  
the diffraction chamber; 7) additional chamber for taking elec-  
tronograms at a short distance; 8 and 9) photo chamber with  
photo holder.

In most cases the electron gun in the modern electronograph consists of an external glass or vacuum cylinder, within which the cathode system is mounted on its upper part and the anode system on its lower part. The former is a metal cylinder, in which is fastened the filament which is the source of electrons. The filament is made of tungsten wire 0.1 mm in diameter in the shape of an acute angle V. The lower end of the cylinder is covered with a cap, the bottom of which has a concave hemispherical form with an aperture 0.1 mm in diameter. This aperture (the cathode diaphragm) is the primary source of electrons in some electronographs. The end of the filament should almost touch the inner surface of the bottom of the cylinder and lie at the center of the diaphragm. For precise installation of the filament of a sif'fon (siphon?) mechanism is used, which moves it up and down along the vertical axis of the instrument and to the right and left in the horizontal plane. The concave hemispherical surface of the bottom of the cap, by creating equipotential surfaces of approximately the same form when an accelerating voltage is applied in the space between the cathode and the anode, partially focuses the electrons emitted by the filament and passing through the cathode diaphragm. In some guns an additional negative potential relative to the filament is applied to this cap. In this case the diameter of the cathode diaphragm is 3-4 mm, and the intensity of the beam and focusing power of the cap

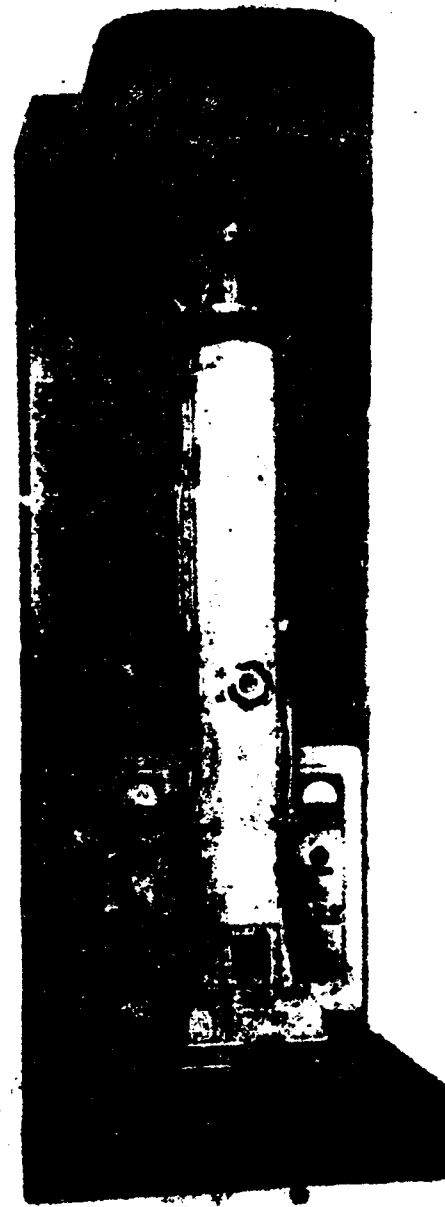


Figure 6. General View of VEIN-1 Electronograph

are considerably increased.

The anode part of the gun is a cup-shaped half-cylinder with thick walls (usually of copper to carry off heat), in the bottom of which is fastened the anode diaphragm (or diaphragm tube with two diaphragms). This half-cylinder is joined either with the lower part of the gun, with the flange uniting it with the condenser system (in the case of glass guns), or directly with the condenser (in the case of porcelain guns).

The size of the aperture of the anode diaphragm may be 50-100 mk, if they are the primary source of electrons, or 2-3 mm, if the apertures in the cathode diaphragm serve as this source.

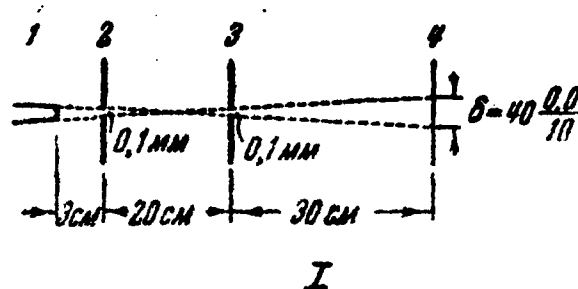
The anode part of the gun, as well as the whole body of the electronograph, is grounded. To render the cathode and anode diaphragms coaxial, the cathode cylinder or the anode diaphragm is made movable by means of a sil'fon (?) in two mutually perpendicular directions in the horizontal plane. In designing the electron gun (32), it is necessary to take into account the fact that the electron beam formed in it by means of the diaphragms and the focusing cylinder was of great intensity and had a small diameter at the level of the aperture diaphragm of the focusing lens. The solution of this problem encounters great difficulties, consisting in the fact that in order to obtain a point source and small electron beam size, one has to use diaphragms with small apertures, which greatly reduce the intensity and still produce a divergent beam.

The divergent beam is poorly focused by the lens, since its spherical aberration is directly proportional to the cube of the radius of the beam at the level of the middle of the non-magnetic clearance of the lens. To reduce this aberration it is necessary to limit the beam by a diaphragm with an aperture of small diameter (~100-100 mk), placing it in the middle or above the non-magnetic clearance of the lens. In this manner, the electron gun, both in the modern electronic microscopes and in the electronographs, does not produce electron beams with a sufficient degree of intensity and small diameter at the level of the lens. When the size of the primary source of electrons is 100 mk at a distance of 30 cm from it, the size of its image on the screen or at the level of the lens will be 400 mk (Fig. 7).

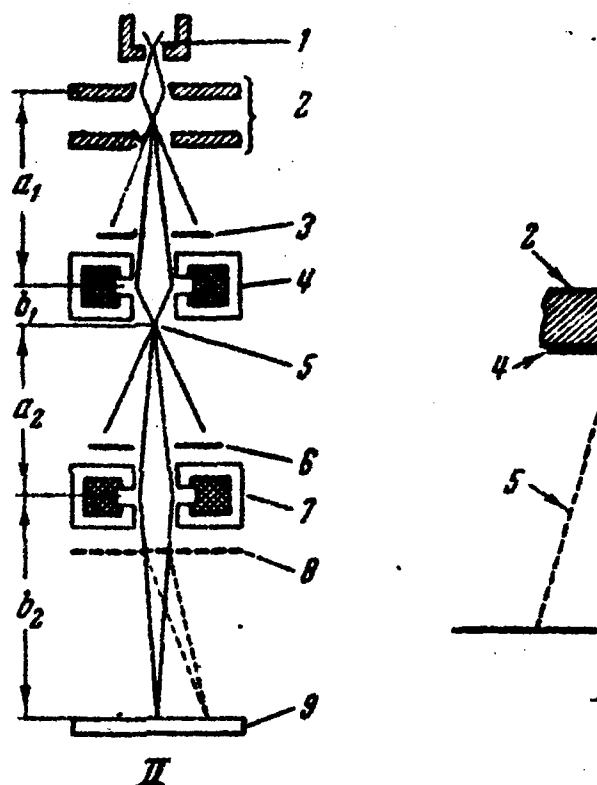
The second important node in the electronograph is the electromagnetic focusing system, consisting of one or two lenses. By means of the focusing system, the electron beam is definitively formed in its width at the level of the sample and in sharpness on the screen or photo plate. The magnetic focusing system must not reduce the intensity of the electron beam formed by the gun, and must not produce an enlarged image of the primary source of electrons on the screen or photoplate.

### Legend:

- I. Path of Electron Beam to Lens:  
 1) filament;  
 2, 3) diaphragms;  
 4) size of beam  $b$ .



- II. Scheme of Arrangement of Electronic Optical Elements and Path of Rays in Electronograph with Two-lens Condenser:  
 1) filament;  
 2) first and second anode diaphragms;  
 3, 6) diaphragms;  
 4, 7) lenses;  
 5) effective source of electrons;  
 8) sample;  
 9) screen.



- III. Scheme of Path of Rays When Photographing Simultaneously for Reflection and Passage of Rays:  
 1) sample;  
 2) thin film of aluminum;  
 3) diaphragmed rays from massive sample;  
 4) diaphragmed rays from aluminum film;  
 5) photo plate.

Figure 7

In the case of the one-lens focusing system the lens is placed at an equal distance  $a$  from the primary source of electrons and from the screen  $b$ ; then it will not produce an enlargement ( $x = b/a$ ) of the size of the primary source. In modern electronographs, the distance from the lens to the screen is 35-70 cm. Consequently, in order to avoid enlargement of the image of the sample by the lens, the distance from the primary source of electron

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the aperture diaphragm of the lens must be of the same order. However, with this distance the diameter of the beam will be so large that it will make it necessary to limit the beam by means of a new diaphragm in front of the lens. The significance of this diaphragm consists in that it prevents the electrons reflected at different angles from the walls of the tube of the electronograph or inner cylinder of the lens itself from getting into the lens (see Fig. 7).

As regards the two-lens focusing system, there are great possibilities of obtaining a small-sized electron beam on the screen. In most cases the lenses are arranged as shown in Fig. 7: the supplementary lens is located at the center between the anode diaphragm and the objective lens (located at the object). The first lens produces a reduced image of the primary source of electrons on the optical axis between the first and second lenses. This image of the primary source will be the secondary, or, as it is usually called, the effective electron source. Its size may be very small, depending on the degree of reduction ( $a_1/a_2$ , see Fig. 7) of the first lens. Thus, for example, with a 50-power reduction the image of a primary source with a size of 100 mk will have a size of 2 mk. However, the second lens in this case will produce on the screen an image of the effective source that is magnified as many times as the distance  $b_2$  is greater than  $a_2$ . Hence, the radius of the beam  $\delta$  on the screen will be:

$$\delta = r_1 \frac{b_1}{a_1} \frac{b_2}{a_2}, \text{ where } r_1 \text{ is the radius}$$

of the primary source, and  $\frac{b_1}{a_1}$ ,  $\frac{b_2}{a_2}$  are the magnifications by the first and second lenses respectively.

It follows from this expression for the size of the beam that with one and the same values of  $r_1$  and  $\frac{b_1}{a_1}$  the size of the beam on the screen will vary proportionally to  $\frac{b_2}{a_2}$ .

By keeping the distances  $a_1$  and  $b_2$  constant and changing only  $b_1$  and  $a_2$  by altering the strength of the current in the first lens, it is possible to obtain on the screen electron beams of sufficient intensity with a size from 6-20 mk. However, the electronograms obtained with two-lens electronographs from thin films of metals or oxides have a considerably lower intensity of the diffraction lines as compared with those taken with one-lens electronographs.

Thus, the modern two-lens electronographs, while possessing considerably better resolving power than the one-lens ones, are considerably inferior to the latter in the intensity of the diffraction pictures. For this reason, electronographs with a two-

the inter-plane distances  $\Delta d = d_1 - d_2$  -- a change of the magnitude of  $\Delta d$  in the radii of the nearest diffraction rings (for poly-crystal substances).

Because of this well-defined agreement between the magnitudes  $d$  and  $\Delta d$ , the resolving power of the electron microscope is determined numerically from the ratio  $\frac{\Delta d}{d}$  or the corresponding ratio  $\frac{\Delta R}{R}$ .

Thus, by the resolving power of a given instrument it is meant the minimum value of the difference between the inter-plane distances of the lattice of the crystals of a given substance, for which the reflections from the corresponding atom surfaces ( $d$  and  $d \pm \Delta d$ ) are separated in the electronogram, i.e., the radii of the nearest two diffraction rings corresponding to these planes are still distinguishable.

The width of the diffraction lines is determined by the size of the image of the primary source of the electron beam on the screen. The size of the primary electron source is fixed by the electron gun, but in most cases, in electronographs in which no additional negative voltage is applied to the focusing cylinder in the gun, an aperture 0.1 mm in diameter in the cathode or anode diaphragm serves as the primary source of electrons.

In cases where additional negative tension [voltage] is applied to the focusing cathode cylinder, the size of the effective primary source of electrons may be determined approximately from the width of the diffraction lines of the electronogram of any substance employed as a standard (thin films of Al, NaCl, etc.). In obtaining standard samples in the form of thin films by the method of evaporation and condensation in a vacuum it must be borne in mind that the size of the crystals in the poly-crystal film depends essentially on the melting point of the given substance, if the condensation of this substance takes place on an underlay at room temperature. Thus, for example, for titanium and zirconium, the size of the crystals in the film is less than 50 Å, while for magnesium and aluminum it is 200-300 Å.

In the ideal case, without allowing for corrections for the aberration of the lenses and the effect of the size of the crystals, the size of the electron beam  $\eta$  on the photo plate will be  $r_1$  of the aperture of the cathode or anode diaphragm multiplied by the enlargement of the condenser:

$$\eta = r_1 M, \quad (2)$$

where  $M = \frac{b}{a}$  is the enlargement of the condenser; and  $r_1$  the radius of the aperture.

The spherical and chromatic aberration of the condenser enlarges the size of this image. An especially great enlargement of the size of the spot is observed in dependence on the size of the crystal.



The expressions whereby the magnitudes of the expansion of the spot for the above reasons are calculated are given in (35). Thus, according to the data in this work, the size of the expansion of the spot, owing to spherical aberration, is:

$$\Delta_{\text{spher.}} = Cb \left( \frac{r_a}{a} \right)^3, \quad (3)$$

where C is a constant;

a and b are the distances from the lens to the primary source and screen, respectively;

$r_a$  is the radius of the opening of the aperture diaphragm of the lens

The size of the chromatic aberration  $\Delta_{\text{chr.}}$  caused by the change in the length of the electron wave owing to the fluctuation of the accelerating voltage V is determined from equation (1):

$$\Delta_{\text{chr.}} = \frac{\Delta V}{2V} \quad (4)$$

The size of the expansion of the spot in dependence on the size of the crystals  $\Delta_{\text{cr.}}$  is determined from the expression

$$\Delta_{\text{cr.}} = \frac{\lambda L}{l} \quad (5)$$

where  $\lambda$  is the length of the electron wave;

L the distance from the sample to the screen;

l the size of the crystals.

It follows from this expression that the expansion of the spot for a given mean crystal size depends very greatly on the magnitude of  $\lambda L$ , i.e., the constant of the electronograph.

One more correction is introduced, due to the fact that the diffracted ray comes into focus in the form of a spherical surface with its center in the plane of the sample. Hence, for a given diffraction ring of radius R, the point of focus will be somewhat above the plane of the screen, so that instead of a point there is formed a disk whose size  $\Delta_R$  is determined from the equation

$$\Delta_R = r_a \left[ 1 - \frac{L}{(L^2 + R^2)^{1/2}} \right]. \quad (6)$$

Thus, allowing for all these corrections, the size of the image of the primary source on the screen will be

$$\eta' = r_{im} + \Delta_{spher.} + \Delta_{cr.} + \Delta_R + \Delta_{cr.}$$

It is evident that the minimum separation of the diffraction rings in the electronogram will be determined by the distribution of the intensity both in the spot and over the width of the ring dependence on the radius of the spot  $\eta'$  or the half-width of the ring. Work (35) gives the following expressions for minimum section and accordingly for resolving power:

$$\Delta R = 1.4 \cdot \eta' \quad ; \quad \frac{\Delta R}{R} = \frac{1.4 \cdot \eta'}{R}$$

Substituting in expression (8) the values of  $R$  from formula (1) and from identity (?), we obtain the final equation for resolving power of the electronogram in the form:

$$\frac{\Delta R}{R} = \frac{1.4 \cdot d}{\lambda L} (r_{im} + \Delta_{spher.} + \Delta_{cr.} + \Delta_R + \Delta_{cr.})$$

The dispersion power of the electronogram is determined by the ratio  $\frac{\Delta R}{\Delta d}$ , where  $\Delta R$  is the difference between the radii of the diffraction rings in the electronogram, and  $\Delta d$  is the difference between the values of the corresponding inter-plane distances.

The dispersion is found from equation (1)  $R = \frac{\lambda L}{d}$  and

$$\Delta R / \Delta d = -\lambda L / d^2.$$

It follows from this equation that the dispersion power and its absolute value with the assigned electron wave length is directly proportional to  $L$  and inversely proportional to the square of the inter-plane distances.

The electron wave length  $\lambda$  in a first approximation is determined by the equation  $\lambda = 12.25 / \sqrt{V - \frac{1}{2}}$ , where  $V$  is the accelerating voltage. With the tensions used in electronography practice, 10-40-70 KV, it varies from 0.06-0.046 Å, i.e., it has practically little effect on the size of the dispersion. The magnitude of the linear dispersion varies from 35-70 cm. There is an especially great variation in the linear dispersion from the values of the inter-plane distances and that in the direction of a decrease in it. Thus, for example, with a change from 1 to 5 Å in the inter-plane distances, the dispersion diminishes 25 times.

It is evident that such a rapid diminution of the dispersion power in dependence on the growth in the inter-plane distances

be compensated either by the magnitude  $\lambda$  or by the magnitude  $L$ . Moreover, for values of  $d$  equal to 10 and 20 Å, the radii of the corresponding diffraction rings computed from the equation

$R = \frac{\lambda L}{d}$  will be, respectively, 3.5 and 1.75 mm, with  $\lambda = 0.05$  Å

and  $L = 700$  mm. But it is known from practice that the diameter of the central spot formed by non-coherently diffused electrons on the photo plate varies from 3-20 mm.

Thus, the diffraction rings corresponding to inter-plane distances of 10 Å or more, even for an electronograph with  $L = 700$  mm, will fall in a strongly lighted (dark) spot on the photo plate and will not be detected.

To heighten the dispersion power of the electronograph, two- and three-lens diffraction chambers have recently (36) begun to be used. This instrument enables one to obtain electronograms with diffraction rings of such diameters as could be obtained in the case of the ordinary electronograph only with a distance of 4500 mm from the sample to the photo plate. Thus, the three-lens diffraction chamber in this case has made it possible to enlarge the dispersion 7.5 times.

The productivity of the electronograph, determined by the number of photos per unit of time, depends on the speed of reaching the vacuum limit and on the number of photos per evacuation, and also on the time taken by the photographing itself and the reloading. The rate of evacuation of the electronograph at present is such that the vacuum limit of  $10^{-4}$  mm mercury is reached in 4-5 minutes with continuously operating pre-vacuum and diffusion pumps. The original exhaustion with the pre-vacuum pump and the warming up of the diffusion pump last 20-25 minutes. If the photo holder contains 12 photo plates, 12 pictures 9 X 12 can be obtained in 5 minutes with exposures of 1-5 seconds from samples for passage of rays or in 10 minutes from 3 samples for reflection and 6 samples for passage. Thus, in 30-35 minutes it is possible to evacuate the electronograph to the working vacuum and obtain 12 pictures. The reloading of the holder and the developing of the plates are done during the next evacuation.

In the Soviet Union, three models of modern electronographs have been developed and successfully used: the EM-4, the model of the Institute of Crystallography of the Academy of Sciences USSR (EG) and the model of the Institute of Metallurgy of the Academy of Sciences USSR (VEIM-1), which is an improved form of the model of the Institute of Physical Chemistry of the Academy of Sciences USSR (37).

Table 1 gives the values of the basic parameters of the electronographs. In all three, the rates of evacuation and the current and tension [voltage] stability of the sources of power are approx-

Table 1

Основные параметры электронной оптики (1)	ЭМ-4 (2)	ЭГ (3)	ЭВИМ-1 (4)	Английский электронограф (35) (5)
$r_0$ , мм	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$2,5 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$
$a$	350	560	500	500
$b$	500	780	550	560
$m$	1,40	1,40	1,10	1,9
$L$	500	700	500	400
$V$ , кВ; $\lambda$ , Å	45; 0,058	75; 0,045	50; 0,055	50; 0,055
$\lambda/L$	20,00	31,5	27,5	22
$r_0/m$	$7 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	$2,75 \cdot 10^{-2}$	$3,8 \cdot 10^{-3}$
$\lambda/L$	0,145	0,160	0,140	0,11
$\bar{L}$	$3,4 \cdot 10^{-3}$	$3,1 \cdot 10^{-3}$	$1,4 \cdot 10^{-3}$	$2,4 \cdot 10^{-3}$
$\Delta R/R$	$1,10^{-2}$	$1 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	$1 \cdot 10^{-2}$
$\Delta R/\Delta d$	20	31,5	27,5	22

LEGEND: 1) Basic parameters of the electronic optical parts;  
2) EM-4; 3) EG; 4) EVIM-1; and 5) British electronograph (35).

[NOTE: Text of article speaks of "VEIM-1"; whereas above in the table is mentioned the EVIM-1.]

imately the same. The mechanism and the possibility of displacing the filament and the gun itself are also approximately the same. Nor do the mechanisms for controlling the displacement of the sample differ substantially. However, each of these electronographs has its characteristic peculiarities. Thus, the EM-4 electronograph is a compact small-sized apparatus, in which the electronograph column and the high-voltage and low-voltage feeding units are assembled in a single bank (blok). An opening with a radius of 0.05 mm in the bottom of the focusing cylinder serves as the primary source of electrons. The condenser consists of two lenses, but practically only one is used, since in operating with both lenses the intensity of the diffraction rings in the electronogram is so small that it does not lend itself to interpretation. The photo holder of the instrument permits one to take 12 pictures 6 X 9 cm in size per evacuation. Among the substantial defects of this model must be mentioned first and foremost the inadequate size of the diffraction field.

The electronograms obtained from the EM-4 instrument with tension of 40 KV and a maximum possible ring radius of 40 mm do contain reflections corresponding to inter-plane distances of less than 0.75 Å. A great defect in the design of this instrument, as well as in the similar US model released in 1946 (41), is the downward displacement of the electron gun, and the upward displacement of the diffraction chamber and the photo chamber. With this arrangement of the main nodes of the electronograph, the openings of the diaphragms quickly get clogged up. Moreover, the parts of the electron gun joined together by picoin [picene?] are in a hanging position in immediate proximity to the electric furnace of the pump. In the absence of additional heat insulation between the gun and the furnace, the glass vessel with the cathode part can separate from the anode part, so that at 50-60 degrees the picoin softens and loses its strength.

The EG electronograph is a horizontal model with respect to the location of the nodes and is more perfect than the former one from this institute. The main change in its design consists in the distance from the object to the photo plate has been reduced from 1400 to 700 mm. A prime defect is the great distance from object to the photo plate (700 mm), which has caused the distance from the electron source to the lens (560 mm) to be increased as to obtain the ratio  $\frac{b}{a} = 1.4$ . Furthermore, at a distance of 560 mm, the cross section of the beam is large (1.5 mm), so that it is necessary to limit it with a diaphragm having a diameter of 1 mm in front of the lens, which diminishes its intensity. The horizontal position of the nodes makes it necessary to join them together in the vertical and horizontal planes; in addition, the electronograph is subject to strong vibration from the pre-vacu-

pump and other vibration installations in the building. Another substantial defect is the use in this instrument of a pocket photo holder which allows only two pictures 9 X 12 cm in size to be obtained during one evacuation, thus considerably lowering the productivity (six times).

The new vertical VEIM-1 electronograph is a small-sized model (A. A. Konstantinov, V. G. Bogdanov, and V. S. Rybakov took part in developing this model), in which the column of the instrument and the electric feed unit are assembled in a single common bank. The primary source of electrons is the anode diaphragm with an aperture of 50 mk. The distance  $a$  from the electron source to lens is 500 mm, while the distance  $b$  from the lens to the screen is 550 mm. The  $b/a$  ratio is 1.1. Thus, the size of the electron beam is enlarged only insignificantly on the screen. The resolving power of the electronograph exceeds by more than twice that of models EM-4 and EG.

The object chamber permits samples to be obtained by the method of evaporation and condensation in the instrument itself in the form of thin films of metals and alloys and other substances, and also allows the thermal and chemical treatment of these films and of massive samples. The holder allows three samples to be installed when photographing for reflection (plates 20 X 10 X 2 cu mm in size) and 6-8 samples or 10-12 samples in the form of thin films for photographing for passage of rays. The electronograph permits the taking of 12 electronograms of 10-12 samples during one evacuation (30-35 minutes), i.e., the structural data on the phase and chemical composition of the oxide film for 8-10 points on the kinetic oxidation curve of metals or data on the phase composition of the metal, oxide, and other systems for several temperatures. The productivity of the VEIM-1 electronograph is six times as great as that of the EG. It is evacuated directly from the photo chamber, the object chamber, and the electron gun by means of nozzles connected with the main tube, which reduces the probability of the spread of water vapor and various gases from the photo plates and samples into all nodes of the instrument and especially into the electron gun.

The table gives the maximum possible accelerating voltages and the corresponding electron wave lengths of the different electronographs. It does not show the values of  $\Delta_{sph.}$  and  $\Delta_R$ , since even for lens aperture diaphragms of 0.50 mm radius, they are  $10^{-4}$  and  $10^{-3}$  mm respectively. With a primary electron source of radius  $5 \cdot 10^{-2}$  to  $5 \cdot 10^{-2}$ , these magnitudes may be disregarded.

The great enlargement of the radius of the spot (and consequently of the width of the lines), caused by the size of the crystals, as may be seen from the table, reduces the resolution by a whole order, and the less the value of  $l$ , the greater the reduction. But despite this it is necessary that the natural half-width of the lines or the size of the spot on the screen from the electron beam should be as small as possible.

The size of the beam is of especial importance in investigating the size of small crystals. The resolving power, without and with allowance for the effect of the size of the crystals, is determined respectively by the following expressions:

$$\frac{\Delta_R}{R} = \frac{1.4 \cdot d}{\lambda L} \cdot r_i \frac{b}{a} ; \quad \frac{\Delta_R}{R} = \frac{1.4 \cdot d}{\lambda L} \left( r_i \frac{b}{a} + \frac{\lambda L}{1} \right).$$

The values of  $\Delta_R/R$  given in the table are computed from the above expressions for  $d = 1 \text{ \AA}$  and  $l = 200 \text{ \AA}$ . The values of the dispersion power are given for  $d = 1 \text{ \AA}$ . It follows from the table that the resolving power of the VEIM-1 electronograph is half again as high as that of the EM-4 and the EG, while the dispersion power

of all four instruments is almost equal. The difference in resolving power is to be explained chiefly by the fact that the size of the beam on the screen is 2.5 times smaller in the VEIM-1 than in the EM-4 and the EG. This is accomplished by reducing both the size of the primary beam and the  $\frac{b}{a}$  ratio, which is reduced to a minimum in the VEIM-1. Further raising of the resolving power for electronographs with a one-lens condenser is obviously possible only by diminishing the size of the primary source of electrons.

Our experience with the electron beam having a 50 mk diameter (diameter of the aperture of the anode diaphragm) confirms this possibility. With this size of beam and the values  $a = 500$  and  $b = 550$  mm, it is possible to achieve a high resolution and entirely adequate intensity of the diffraction picture. In the modern electronographs with two-lens condensers, no success has been had in obtaining a satisfactory combination of these two parameters. The small differences in the dispersion power of all the instruments, despite the different distances  $L$  (varying from 400 to 700 mm), are to be explained by the fact that the magnitude  $L$  enters into the formulas both for the resolving and for the dispersion power in the form of a product with the magnitude  $\lambda$  -- the electron wave length, which, as is known, is inversely proportional to the square root of the accelerating voltage. In increasing the distance  $L$  to 700 mm, the distance from the primary source of electrons to the lens also has to be increased to 560 mm in order to preserve the ratio  $\frac{b}{a} = 1.4$  (which occurs in the EG instrument). Here, the total distance from the source of electrons to the screen ( $a + b$ ) is increased to 1340 mm. Since the electrons pass through this distance by inertia and the vacuum in the electronograph is  $10^{-4}$  of mercury, it is necessary to raise the accelerating tension considerably in order to diminish the divergence of the beam in the space of the first lens and the losses of electron velocity due to the collision of electrons with molecules of residual gas and lubricant vapor in the instrument. However, an increase in the accelerating voltage diminishes the electron wave length, so that the product  $\lambda L$  (constant of the instrument) is not increased much.

Thus, increase in the distance  $L$  from the object to the screen cannot alone achieve a substantial raising of both the dispersion and the resolving power. For electronographs with a one-lens condenser the following basic parameters may be recommended:

- 1) Diameter of the opening in the cathode protecting and focusing cylinder, 0.5-1 mm;
- 2) Diameter of the opening in the anode diaphragm, 50 mk (primary source of electrons);
- 3) Distance from the anode diaphragm to the aperture diaphragm of the condenser,  $a = 450-500$  mm;
- 4) Diameter of the opening of the aperture diaphragm, 0.5-0.6 mm;

- 5) Distance from the last diaphragm to the screen, 550 mm
- 6) Distance from the object to the screen, 500 mm.

#### METHOD OF MAKING A PHASE ANALYSIS

As noted above, the atomic structure of oxides is determined by electronographic analysis. The possibility of successfully using the electronographic method for quantitative phase analysis was shown recently by L. S. Palatnik and B. T. Boyko (42, 43) in investigating the process of decomposition of an over-saturated solid solution in thin films of alloys with an aluminum or copper base. The authors found an original solution for the problem of obtaining two displaced electronograms on one and the same plate from two standard samples (for example, from Al and  $\text{CuAl}_2$  in the case of the system). The displaced and superimposed electronograms were obtained by the periodic displacement of the primary electron beam from sample to the other by means of divergent plates (placed between the source of electrons and the object), to which electronographic impulses of voltage of the rectangular form were applied. By changing a definite length of the impulse or its frequency, one can superimposed electronograms having the necessary ratio of intensities between the comparable lines on the basic and displaced electronograms. According to the authors' data, the impulses were applied with a frequency of 10,000 cycles, which with a 1-2 second exposure are identical conditions for obtaining electronograms of both standard samples.

The ratios of the volume concentrations of the phases in the alloy were determined by comparing the intensity of the lines in the standard superimposed and in the electronogram of the two-phase alloy (mixture of the phases: Al +  $\text{CuAl}_2$ ). The precision of the agreement between the data of the electronographic phase analysis and the data computed by the S. A. Vekshinskiy method is 2%.

This method of obtaining superimposed electronograms can be used for massive samples if the phases do not have a laminar distribution. In case of thin films, a laminated arrangement of the phases in the alloy is also possible. Here it is necessary to see to it that the thickness of the films and the size of the crystals in them are alike both for the standard sample and for the sample under study. In both cases, one should use the electronographic method of investigating the secondary (crystallite) structure of the objects.

The technique of making a high-grade electronographic phase analysis of the drosses is fairly simple, if electronograms with sharp diffraction lines are obtained from the samples under study and the dross itself consists of oxides with known structures.



The first stage of analysis consists in determining the constant of the instrument  $2\lambda L$  by the formula:

$$2\lambda L = dD,$$

where  $D$  is the diameter of the diffraction ring, in mm; and  $d$  is the value of the inter-plane distance from the standard substance corresponding to this ring, in Å.

One of the phases of the given sample may be used as the standard substance. For example, as regards the oxidation of thin films of metals or their solid solutions, the standard may be the gradually oxidizing metal. The value of the constant of the instrument is then determined from the above formula as the mean between three strong lines of the metal; in choosing the lines, preference must be given to those which have a large diameter. For rings with large diameters, the relative error  $\Delta D/D$  of measurement of their diameter will be less than for rings with small diameters. To determine the constant of the instrument one may select diffraction rings in the electronogram with 30-50 diameters. The relative error will then not exceed 0.2-0.3% when the ring diameter is measured with a precision of 0.1 mm.

If the phase composition of the dross is determined from samples in the form of thin laminas deposited from aqueous (or other) suspension on underlays, table salt, introduced into the aqueous suspension in the quantity of 0.1-0.05%, is mostly used as the standard substance.

Thin films of metals, used simultaneously as underlays, may also be employed as standards. For this purpose, thin films of aluminum are widely employed, being easily obtained by the method of evaporation and condensation in a vacuum, and the electronograms of them contain sufficiently sharp lines to determine the constant of the instrument.

It is considerably harder to determine the constant of the instrument from electronograms obtained from massive samples by the reflection method, since it is very difficult to obtain simultaneously on one and the same photo plate a diffraction picture of the standard and of the surface of the sample under investigation. Hence, the most common practice is to take an electronogram of the standard some time after obtaining one for reflection, it being possible to obtain both electronograms on one and the same plate, as well as on different ones. When the high tension is well stabilized (0.01-0.03%), this method of determining the constant is fairly reliable. One may also use the method of simultaneously taking electronograms on one and the same plate from the sample under study for reflection and from the standard (aluminum film) for passage of rays (the author has been applying this method since 1952). For this purpose, the thin film of aluminum deposited on the grid is arranged on the

In quantitative analysis, a visual relative evaluation of the intensity of the lines by the 9-point scale is mostly sufficient.

In evaluating the intensity, account must be taken of the uneven distribution of the background intensity in the electronograms, especially when underlays of the cellulose type are employed. In many cases, such a strong background in the area of the central spot is observed in the reflection electronograms of massive samples that even the high-intensity diffraction rings are not revealed in it. Hence, for the central part of the diffraction picture, it is necessary to make a shorter exposure than for a peripheral picture, and both parts must be photographed separately.

The multiple-exposure method (45) usually employed to evaluate the intensity of the lines from samples for passage of rays can also be used for electronograms for reflection. An accurate and direct precision determination of the absolute values of the intensities can be made by means of meters and photo multipliers with an attachment for the elimination of the background. The method of recording the diffraction picture proposed in (34) permits one to solve this problem in a positive manner.

The concluding stage of qualitative analysis consists in comparing the values of the inter-plane distances computed from the electronograms of the oxide film under study with their values obtained for the presumed oxide (or compound of oxides) by the X-ray method. If it is found in this comparison that the values of  $d$  for three (or more) basic and characteristic lines in the electronogram of the oxide under study having the strongest intensity will coincide with the tabular values of the inter-plane distances with sufficient precision (0.3-0.5% for electronograms for passage of rays and 0.8-1% for reflection electronograms) for lines of the same intensity, the oxide (or other) phase in the dross of the given sample is regarded as established. The task of determining this or that oxide phase is considerably facilitated by the fact that the chemical composition, structure, and thermodynamic characteristics of the given sample are usually known. If an oxide is formed with a new and unknown structure or with a structure whose lattice parameter values deviate considerably from those of the presumed oxide or oxide compound, the means of electronographic and roentgenographic, and in some cases also neutronographic, analysis are employed to determine the crystal structure and establish the nature of the phase from it.

Despite the high absolute sensitivity of the electronographic method of investigation, which permits one to obtain a diffraction picture of  $10^{-12}$  g of a substance, its precision in determining the phase composition of mixtures of oxides and other compounds does not exceed that of the X-ray method and amounts to 1-5%.

In addition to phase analysis of the dross, the electrono-

lower edge of the sample in such a way that the grid with the film is raised 0.05-0.1 mm above the surface of the massive sample under study (Fig. 7, III).

The second stage of phase analysis is the measurement of the diameters of the diffraction rings in the electronograms of the samples in the form of thin films or the radii of these rings in the electronograms of massive samples for reflection. The diameters and radii are measured with an ordinary ruler (preferably with 0.5 mm graduations) with a precision of 0.1-0.2 mm, or with a comparator with a precision of 0.01 mm. The center of the diffraction rings in the ray-passage electronograms is the trace of the central electron beam in the form of a small pit in the photo emulsion and a black dot.

As regards reflection pictures, there is either no such trace at all, or it sometimes fails to coincide with the true geometric center of the half-rings in the electronogram. In such cases, it is useful in finding the center to use celluloid sheets to which 2-3 half-rings can be transferred and to determine the center from them, not from the lines on the electronogram itself. The center of the diffraction picture for reflection may be determined by means of patterns representing the set of rings or half-rings drawn on the celluloid plates with radii computed for the various values of the inter-plane distances at the known value of the constant of the instrument, i.e., from the formula  $D = \frac{2\lambda L}{n}$ . By superimposing the thus constructed picture on the electronogram of any sample, one may, by superimposing two or three rings, determine the center of the half-rings in the electronogram. To find the center, one may use the electronogram of the standard for passage of rays.

Then the inter-plane distances  $d$ , corresponding to the values of the diameters or radii, are computed by the formulas:

$$\frac{d}{n} = \frac{2\lambda L}{D} \quad \text{or} \quad \frac{d}{n} = \frac{\lambda L}{R},$$

where  $L$ ,  $D$  and  $R$  are measured in millimeters, and  $\lambda$  in angstroms.

In more precise calculations of electronograms, the values of  $d$  are computed from the expression:

$$\frac{d}{n} = \lambda \frac{L}{R} \left[ 1 + \frac{3}{8} \left( \frac{R}{L} \right)^2 - \frac{13}{128} \left( \frac{R}{L} \right)^4 + \frac{55}{1024} \left( \frac{R}{L} \right)^6 - \dots \right]$$

The third stage is the determination of the intensity of the diffraction lines. In investigating structures or making a quantitative phase analysis the intensities are determined in the same way as in the X-ray structural analysis: from microphotograms obtained by means of recording microphotometers. The photometric method of determining intensity has been described in detail in (44).

graphic method can be used to determine the orientations of the crystals in the oxide film with relation to the crystals of the metal on the surface of the sample. By studying in detail the orientation relationships between the crystals of the oxide film and the underlying layer of metal (or, in general, the crystals in the surface layer of the underlay, on which the new phase is formed), P. D. Dankov (46) established the principle of "orientation and size agreement." On the basis of this principle, P. D. Dankov (1, 47) and V. I. Arkharov (12) created the foundations of the crystallochemical theory of the oxidation of metals and alloys.

#### ELECTRONOMICROSCOPIC METHOD

The electronmicroscopic method of investigation and the corresponding apparatus have been widely described in a number of monographs and review articles (32, 50, 51). Hence, we shall only deal briefly with the main problems of investigation of the oxidation processes, which can be successfully solved by means of the electron microscope. To these problems belong the following: investigation of the process of the formation and growth of oxide crystals on the individual planes of the grains of the metal; study of the recrystallization processes in oxide films depending on the time and temperature of oxidation; determination of the microfissures and pores in oxide films; investigation of the chemical and phase conversions in the thin free (without underlays) films of metals, alloys, and oxides. The methods and results of the investigation of the mechanism of the formation and growth of primary crystals (nuclei) of oxides on the individual planes of the crystals of certain metals have been described in (52-54).

The recrystallization processes in oxide films on metals and alloys depending on the time and temperature of heating have been studied by the author and his associates. Figures 8 and 9 show electronmicrograms of oxide films formed on metals and alloys at different temperatures and times of exposure. These micrograms were obtained both from lacquer (collodion) and from quartz or carbon replicas.

The first three problems are solved by the replica method, the last by the method of X-ray films having a thickness approximately equal to the size of the crystals in the film.

Replicas of oxide surface films are obtained without any chemical or mechanical treatment of the surface of the sample. Hence, they reproduce the true relief of the oxide film, the size and form of the crystals in it in a form resulting solely from the oxidation process itself. The size of the crystals increases both with the growth of the temperature and with the lapse of heating time, varying from 20-30  $\mu$  at 20-100° to 10<sup>4</sup>  $\mu$  at 1000-1200°.

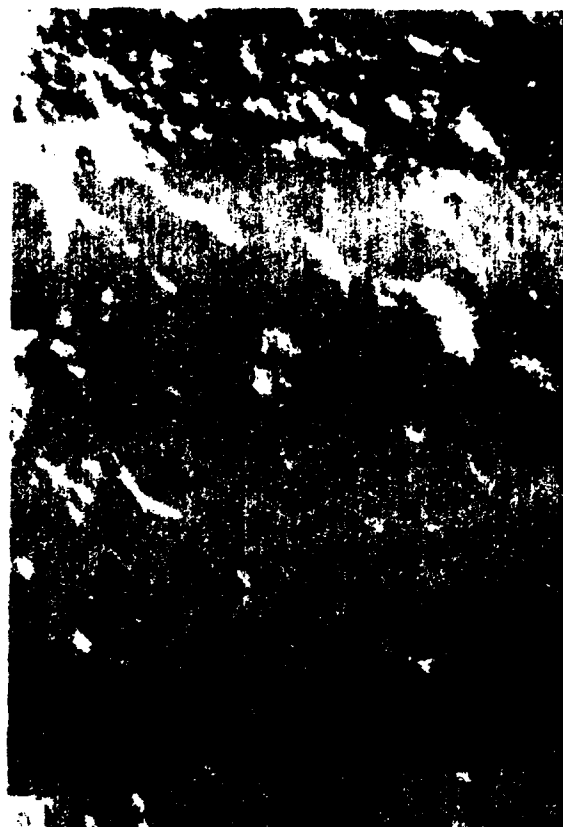
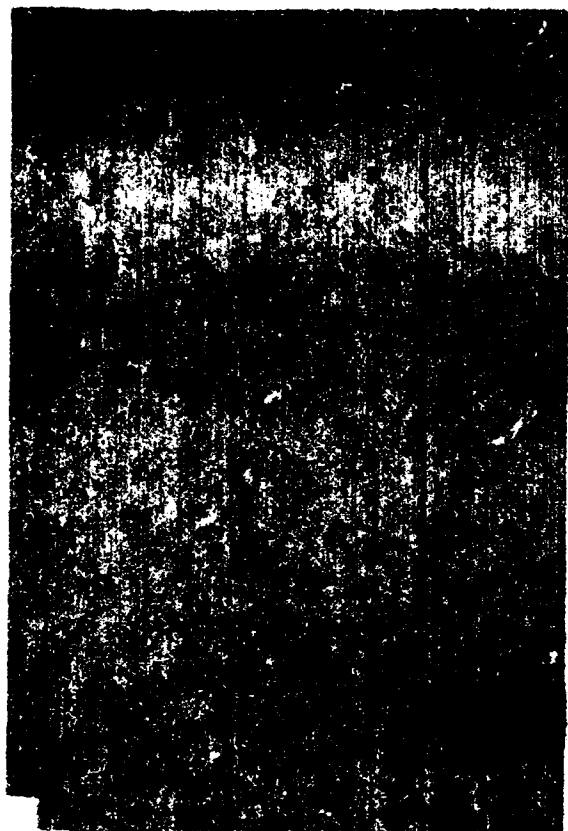


Figure 9. Electron Micrograms of Oxide Films on Chromium Alloys,  
Formed When Heated in Air. a) 600°; b) 700°; c) 900°;  
d) 1000° (X20,000)

The recrystallization process is considerably accelerated and begins at lower temperatures in those cases where the volume of the oxide is 2-3 times greater (for example, for the metals Fe, Cr, Mo) than the volume of the oxidized metal, though such an intensification of the recrystallization process is not observed in thin free (without underlays) oxide films of these same metals. Thus, this effect of accelerated recrystallization of the oxide film for these metals may be explained by the presence of great compression stresses in the dross.

In investigating the kinetics of the oxidation of multiple-component alloys one can observe in some cases that the phase composition of the dross, according to electronographic analysis data, does not vary in dependence on the time and temperature, but the rate of oxidation, determinable by the weight increase, changes sharply from a certain moment on. Thus, for example, in investigating the kinetics of the oxidation of alloys having a nickel or chromium base with addition of boron, such sharp changes in the oxidation rates of this alloy were discovered at a temperature of over  $1000^{\circ}$  in dependence on the time. By means of the electron microscope, pores the size of 20-5000 Å were detected in the dross on the samples. The irregular course of the kinetic curves was connected with the rate of evaporation of the volatile oxides and with the formation of pores (Fig. 9, b and d).

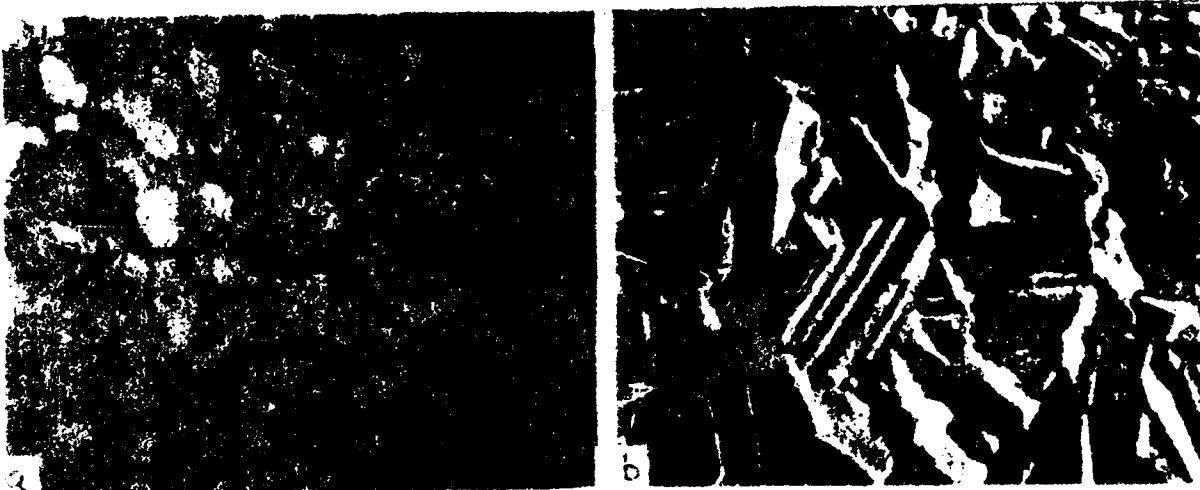


Figure 10. Electron Micrograms of Oxide Films Formed on Nichrome Alloys (X 20,000)  
a) and b)  $900^{\circ}$  for 100 and 1,000 hours respectively;

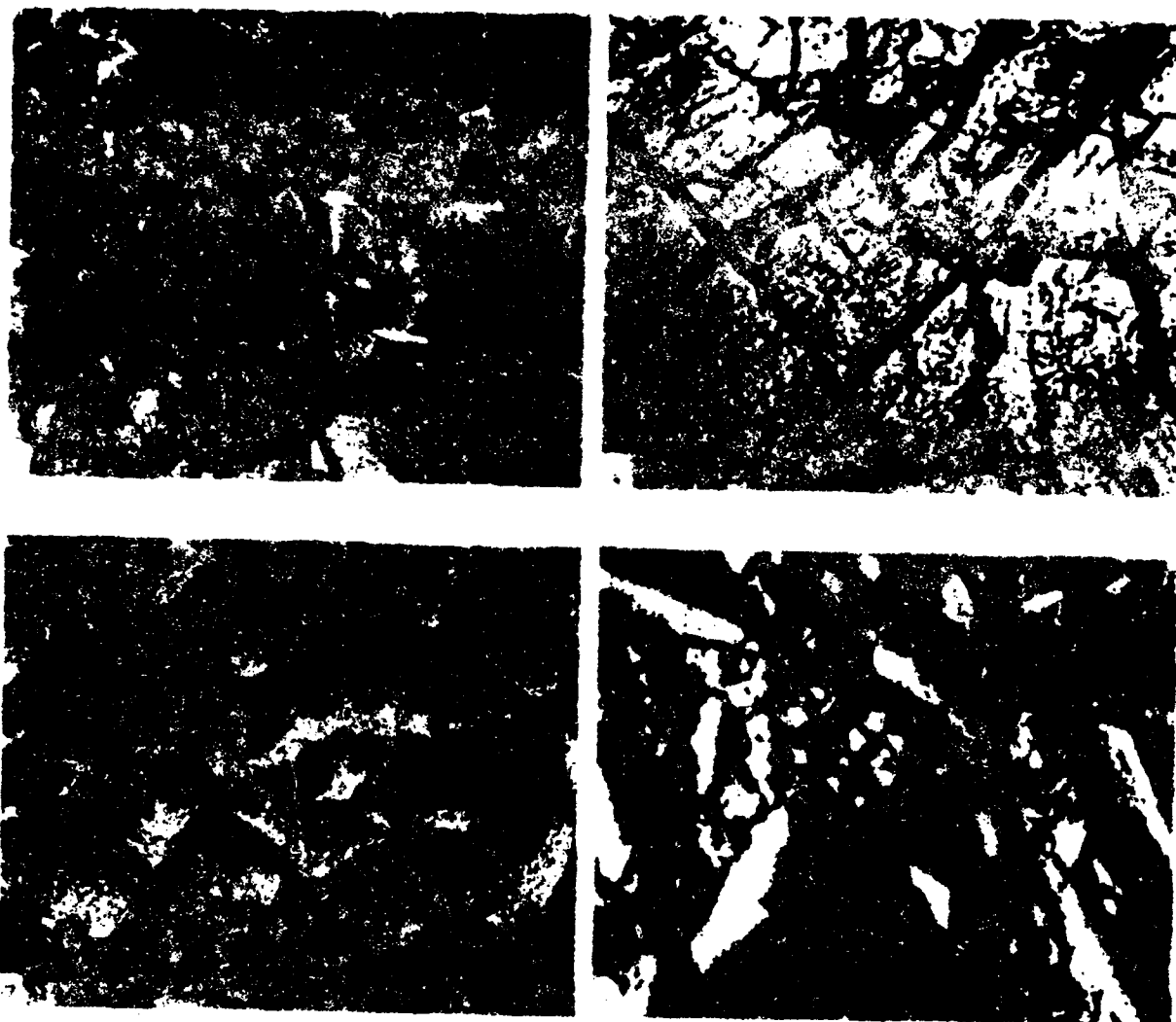


Figure 10. (continued)

c)  $900^{\circ}$ ; d)  $1030^{\circ}$  (with addition of boron) for 100 hours; e) on Ti-V alloy at  $600^{\circ}$ ; and f) on Ni-Cr Alloy at  $900^{\circ}$  for 3 hours.

Fig. 10 [sic. Means Fig. 11, see next page] gives as an illustration electronmicrograms and electronograms obtained by the ray-passage method from one and the same samples in the form of thin films heated in air at temperatures from  $20-900^{\circ}$  at 100-degree intervals. The use of the electron-microscope method for investigating the process of the growth of crystals in thin films is limited, since with a film thickness exceeding by several times the size of the crystals in it, the electron micrograms obtained are unclear

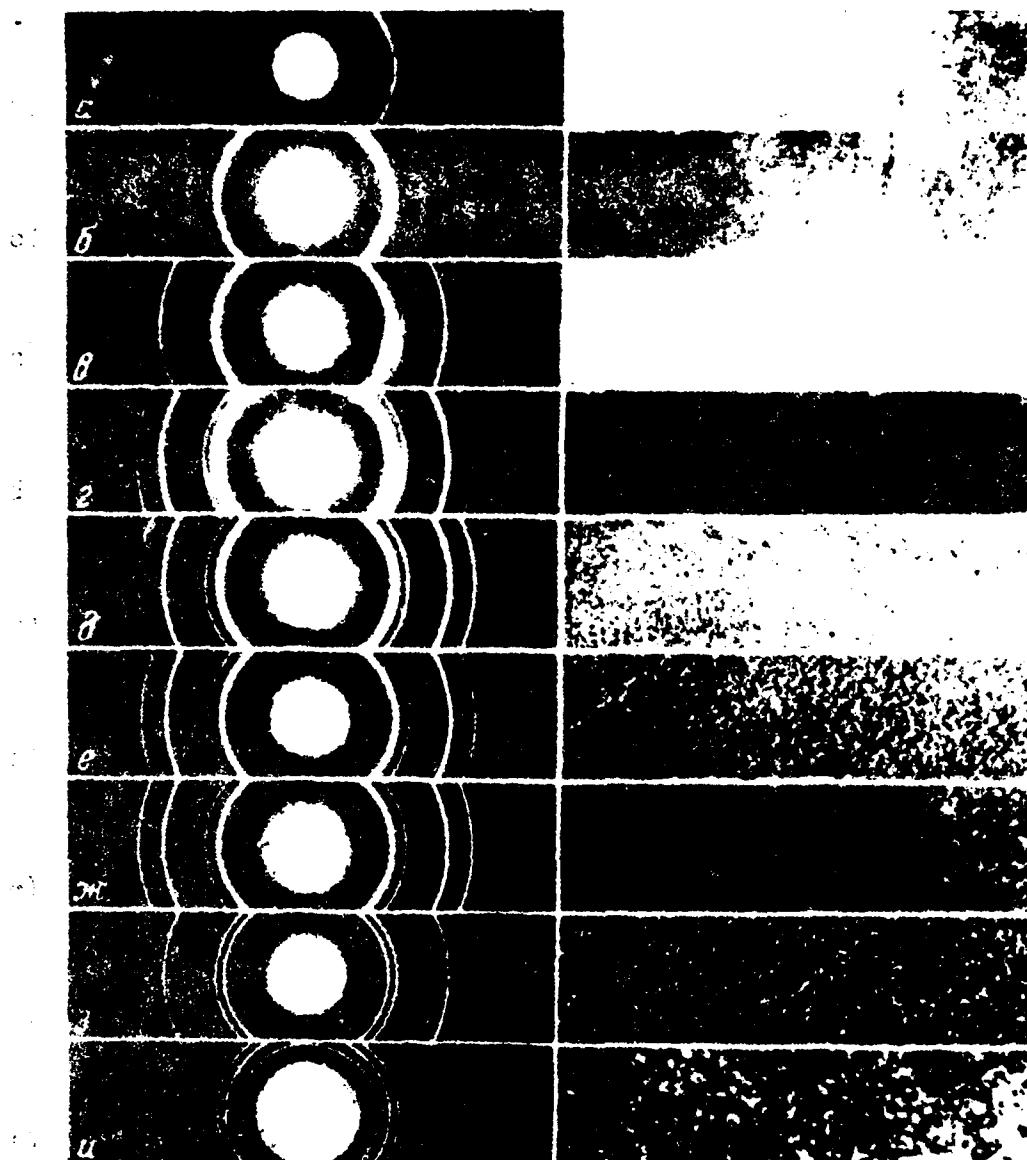


Figure 11. Electronomicrograms (Right) and Electronograms (Left) of a Thin Film of Zirconium ( $\times 20,000$ ), Heated in Air for 1 hour at the Following Temperatures:  
 a)  $20^{\circ}$ ; b)  $200^{\circ}$ ; c)  $300^{\circ}$ ; d)  $400^{\circ}$ ; e)  $500^{\circ}$ ; f)  $600^{\circ}$ ; g)  $700^{\circ}$ ; h)  $800^{\circ}$ ; and i)  $900^{\circ}$ .

because of the superimposition of the image of one crystal upon that of another. Only when the thickness of the film is equal to the mean size of the crystals can one trace in it the change in their forms and sizes in the recrystallization and oxidation processes. The metallographic method can be successfully employed alongside



of the electron-microscope method to detect inter-crystal corrosion, pores, and fissures in the dross, as well as to study the transverse structure of the dross.

#### ISOTOPIC METHOD OF INVESTIGATION

For the isotopic method of investigating oxidation processes, the radioactive isotopes of metals and the stable isotope of oxygen  $O_{18}$  are used. This method determines the parameters of the diffusion coefficient on temperature. By comparing the values of the coefficients of the diffusion of the ions of the metal and of oxygen through the oxide of the given metal, one may ascertain what ions are diffused to bring about the oxidation process. Thus, for example, in determining the parameters of the diffusion of copper and oxygen ions through the oxide  $Cu_2O$  at  $1030^\circ$  (55), it has been established that the coefficient of oxygen diffusion under 135 mm mercury pressure has a value of  $1.3 \cdot 10^{-9}$  sq cm/sec, and the coefficient of copper diffusion  $4.8 \cdot 10^{-8}$  sq cm/sec.

The coefficients of oxygen diffusion in the oxide systems are found by the Zimens method (56) by determining the rate of exchange between the oxygen of the oxide and the gaseous oxygen enriched with isotope  $O_{18}$ . The method of determining the rate of this exchange in dependence on the temperature is described in (57), and the methods of determining the parameters of the diffusion of metals in oxides are described in (58-60). Unfortunately, it is difficult to compare the rate constants and activation energies of the diffusion of the same metals or of oxygen through their oxides, since the oxidation processes of metals are usually investigated at temperatures considerably lower than those at which the diffusion processes are studied. For example, the oxidability of aluminum is investigated in the temperature interval of  $20-600^\circ$ ; that of nickel, cobalt, and chromium,  $20-1000^\circ$ ; that of titanium, zirconium, and niobium,  $20-900^\circ$ . But the diffusion processes of metals in oxide systems with measurable rates take place in a temperature interval of  $1100-1400^\circ$ . At temperatures up to  $1100^\circ$  the borderline diffusion in sintered samples is so intensive that the true values of the parameters of their volume diffusion cannot be determined. During diffusion roastings at high temperatures ( $1100-1400^\circ$ ) there is an intensive evaporation of many metals and certain oxides ( $ZnO$ ,  $Cr_2O_3$ , and others), but also an oxidation of the active layer of metal deposited on the samples by that [oxygen?] which has remained and is secreted from the walls of the ampules of oxygen. In the case of roastings in quartz ampules evacuated to  $10^{-4}$  mm of mercury at  $1100-1200^\circ$ , a perceptible evaporation of  $SiO$  is observed from the walls of the ampules, and a diffusion of oxygen through their walls.

The effectiveness of the evaporation and oxidation is some-

what diminished when the ampules are filled with purified argon up to a pressure of 200 mm of mercury and zirconium iodide is placed in them. The diffusion roastings at temperatures of 1100-1400° should be made in ampules cast of pure aluminum oxide ( $\alpha = \text{Al}_2\text{O}_3$ ) or beryllium oxide. These roastings may also be done in vacuum micro-furnaces introduced into evacuable (or argon-filled) and water-cooled tubes of molybdenum glass (see Fig. 4).

More precise data on the diffusion parameters in the oxide systems can be obtained with fused samples by using iridium crucibles for melting the oxides. To remove the active layers from the oxide samples, the author and V. V. Votnova used tablets of boron carbide 15-20 mm in diameter and 2-3 mm thick, which are pressed from fine powder with the addition of alcohol or water and roasted in the furnace at 600-700° in air. For precision removal of the active layers of the prescribed thickness one may use a micro-tome, replacing the steel knife in it with a plate having tablets of boron carbide mounted in it.

#### SAMPLES AND METHODS OF TREATING THEIR SURFACE

Samples in the form of plates 15 X 10 X 5 mm in size are used to investigate the oxidation processes of metals and especially of alloys by the structural-kinetic method. The last dimension (thickness) may be 3-4 mm. Samples of this form satisfy both kinetic investigations (have a considerably larger surface with relation to the volume than in the case of cylinder-shaped samples of the same volume) and electronographic investigations (a width of 10 mm is obligatory).

The thin films of metals and alloys obtained by the method of evaporating and condensing metals in a vacuum are extremely necessary in investigating the oxidation mechanism. To one degree or another they model the massive samples as to chemical composition and are standards, and, likewise, they permit one in a short interval of time to determine the temperature intervals of formation and decomposition of the various phases both in alloys and in the oxide systems. Moreover, the thin films of metals can be used for precision investigation of the primary stages (adsorption, dissolution, and formation of the oxide phases) of oxidation at low and medium temperatures (from 180-500°) by the monometric and micro-weighing methods. For this purpose, one may employ samples of thin sheet iron or foil 0.05-0.3 mm thick. In all cases of the use of samples in the form of thin films or made of thin sheet iron or foil, one must see to it that the two fronts of the reaction (or limits of the dissolution of oxygen) shifting from the outer limits on the two sides of the sample to its central inner limit are not closed in the oxidation of the plate samples. In the oxidation of thin metal films

the front of the reaction (or limit of dissolution of oxygen) must not approach the surface of the underlay on which this film lies. If this precaution is not taken, the kinetic curves on the weight-increase and time coordinates will have an asymptotic march and an erroneous conclusion may be drawn about the heat resistance of the given metal or alloy.

Treatment of the surface of samples before oxidation is of great importance for the investigation of the kinetics of oxidation. In practice, the following methods of treating the surface are usually used: mechanical grinding and polishing, etching, and electrochemical polishing. A significant shortcoming in the mechanical-polishing method is that, in treating the sample, the surface layer is greatly soiled by the abrasive material and by the particles of the oxide film forming and crumbling away during the polishing. Since the surface of the sample before polishing has narrow and deep depressions in the form of fissures and niches, as well as fine, sharp protrusions, these depressions become filled with paste, grains of the abrasive, particles of metal and oxide film (while polishing with paste or moistened abrasive powder), and the protrusions (of the hangnail type) are pressed against the surface, capturing these products of polishing. Hence, after polishing, the surface layer of the sample will not be metallic, but metallo-ceramic and vitreous, both in structure and luster.

In etching and electric polishing, the metal is soiled with hydrogen and the surface layer soiled by the products of electrolytic corrosion.

These shortcomings can be avoided if the surfaces of the samples are ground on hard (sintered or, preferably, fused) abrasive disks or plates in the form of razor hones. For many metals and alloys, thick (1-2 cm) mirror glasses with different degrees of grinding may be used as such plates, the grinding being done with the powdered abrasives used by glassblowers for grinding and vacuum-resetting of cocks. Boron, titanium, and other carbides sintered with a binder in the form of plates are suitable for grinding the harder metals and alloys.

Polishing of samples on such sintered or fused abrasive plates (previously ground to the necessary degree of roughness) is done in the same manner as with emery paper, but the sample being polished must be moved along a fresh part of the abrasive plate [disk] so as to avoid repeating the old trace. After the whole surface of the abrasive plate has been used, the layer of metal remaining on it is wiped off with a rag moistened with purified alcohol. With this dry-grinding method, the plates themselves are actually not worn out, the grains of abrasive are not torn off them, and, consequently, the surface of the sample is not soiled. The degree of roughness achieved by this grinding is entirely satisfactory both for kinetic

24. J. Langmuir. J. Amer. Soc., 39, 1918.
25. Z. G. Pinsker. Zavodskaya laboratoriya (Plant Laboratory), 24, No 5, 1958.
26. G. J. Finch. Uspekhi fizicheskikh nauk (Advances in Physical Sciences), 20, No 2, 1938.
27. H. Kaether. Erg. der exakten Naturwissenschaften, 24, 54, 1951.
28. Collection Rentgenovskiy metody issledovaniya v khimicheskoy promyshlennosti (X-ray Methods of Investigation in the Chemical Industry), Goskhimisdats, 1953 (under the editorship of G. S. Zhdanov).
29. B. K. Bayshteyn. Strukturnaya elektronografiya (Structural Electronography), Publishing House of the Academy of Sciences USSR, 1956.
30. Collection Sovremennyye metody issledovaniya v metallovedenii (Modern Methods of Investigation in Metallography), Gostekhnizdat, 1958 (translated under the editorship of Ya. S. Umanskiy and V. N. Finkel'shteyn).
31. A. A. Lebedev. Nature, 128, 491, 1931.
32. Collection Elektronnaya mikroskopiya (Electronic Microscopy), GITTL, 1954, (under the editorship of A. A. Lebedev).
33. J. J. Trillat and N. Takahashe. J. Phys. et radium, 14, No 5, 1953.
34. G. O. Bagdyk'yants and A. G. Alekseyev. Annotatsii dokladov 2-go soveshchaniya po elektronnoy mikroskopii (Annotations to the Reports of the second Conference on Electronic Microscopy), Scientific Technical Society of Radio Engineering and Electcommunications imeni A. S. Popov, Moscow, 1958.
35. R. S. Page and R. G. Garfitt. J. Sci. Instr., 29, 1952.
36. N. C. Corbet, M. Ments, J. Kramer, J. B. Le Poole, and L. L. Reisen. Optik (Optics), 12, No 5, 1955.
37. P. D. Dankov and D. V. Ignatov. (Reports of the Academy of Sciences USSR), 54, No 3, 1946.
38. G. O. Bagdyk'yants. Izvestiya Akademii Nauk SSSR, seriya fiz. (Bulletin of the Academy of Sciences USSR, Physics Series), 17, 1953.
39. B. K. Bayshteyn and Z. G. Pinsker. Elektronograf dlya strukturnykh issledovaniy (The Electronograph for Structural Investigations), Publishing House of the Scientific Technical Committee of the Council of Ministers USSR and the Academy of Sciences USSR, 1958.
40. Novaya model' vertikal'nogo elektronografa (VEIM-1) Instituta metallurgii AN SSSR (New Model of the VEIM-1 Vertical Electronograph of the Institute of Metallurgy of the Academy of Sciences USSR), Publishing House of the Academy of Sciences USSR, 1957.

41. J. Hillier and R. F. Baker. J. Appl. Phys., 17, 12, 1946.
42. L. S. Platnik and B. T. Boyko. (Reports of the Academy of Sciences USSR), 120, 1958.
43. L. S. Palatnik, B. T. Boyko, and V. M. Kosevich. (Plant Laboratory), No 4, 1958.
44. I. I. Yamzin and Z. G. Pinsker. (Reports of the Academy of Sciences USSR), 65, 1949.
45. B. K. Vaynshteyn and Z. G. Pinsker. (Reports of the Academy of Sciences USSR), 72, 1950.
46. P. D. Dankov. Trudy II Konferentsii po korrozii metallov (Works of the Second Conference on the Corrosion of Metals), Vol II, Publishing House of the Academy of Sciences USSR, 1943.
47. P. D. Dankov. (Journal of Physical Chemistry), 26, No 5, 1952.
48. V. I. Arkharov, V. N. Bogoslovskiy, B. S. Borisov, and Z. P. Kichigina. Issledovaniya po zharoprochnym splavam (Investigations into Heat-Resistant Alloys), Vol II, Publishing House of the Academy of Sciences 1957.
49. N. A. Shishakov. (Journal of Physical Chemistry), 31, 33, 1957.
50. V. M. Luk'yanovich. Uspekhi khimii (Advances in chemistry), 27, Issue 6, 1958.
51. Yu. M. Kushnir. Pribory i tekhnika eksperimenta (Experimental Instruments and Equipment), No 4, 1958.
52. J. Bardolle and J. Benard. Rec. Met., 49, 1952.
53. J. Moreau and J. Benard. C. R. Acad. Sci., 238, 1954; J. Inst. Met., 83, 87, 1954-1955.
54. E. A. Gulbransen, W. R. Macmillan and K. Andrew. J. Met. A. J. M. E., 6, 1954.
55. J. Moore. J. Chem. Phys., 1957.
56. K. E. Zimens. Arkiv Kemi Miner, 20A, No 18, 1945.
57. Ye. I. Dontsova. (Reports of the Academy of Sciences USSR), 95, No 6, 1954.
58. R. Lindner and A. Akerstrom. Z. Phys. Chem., 6, 1956.
59. A. I. Borisenko and Ye. I. Morozov. (Reports of the Academy of Sciences USSR), 105, No 6, 1955.
60. D. V. Ignatov, I. N. Belokurova, and I. N. Belyakin. Sbornik trudy Vsesoyuznoy nauchno-tekhnicheskoy konferentsii po primeneniyu radioaktivnykh i stabil'nykh isotopov i izlucheniya v narodnom khozyaystve i nauke (Collected Works of the All-Union Scientific Technical Conference on Utilizing Radioactive and Stable Isotopes and Radiations in the National Economy and Science), Publishing House of the Academy of Sciences USSR, 1958.

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